## Supporting Information

# Metal-Free Synthesis of Propargylamines via Light-Mediated Persulfate Activation and Phase-Transfer Catalysis

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## 1. General Information

All reagents were purchased from commercial suppliers (Sigma-Aldrich, Oakwood and Combi-Blocks) and used without further purification, all solvents were analytical grade. Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness, visualization was accomplished with short wave UV light or $KMnO_4$ staining solution followed by heating. Hydrogen nuclear magnetic resonance spectra ($^1$H NMR) were obtained at 500 MHz in $CDCl_3$ solutions, at ambient temperature. Carbon-13 nuclear magnetic resonance spectra ($^{13}$C NMR) were obtained at 125 MHz in $CDCl_3$ solutions, at ambient temperature. Chemicals shifts (δ) are given in ppm and the residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra ($CDCl_3$: $\delta$H = 7.27 ppm, $\delta$C = 77.00 ppm. High resolution mass spectra were recorded on Q Exactive Orbitrap spectrometers working with an electrospray ionization (ESI). The Gas Chromatography coupled to Mass Spectrometry (CG-MS) analyses were performed using a Network GC system 6890N (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with a HP-5MS 5% Phenyl Methyl Silox (25.0 m × 250 µm × 0.25 µ nominal) capillary column. The GC analyses were carried out in split mode (ratio 150:1) using helium as carrier gas at a flow rate of 504 mL/min (7.65 psi). The injection port temperature was 250 °C; the oven was maintained at an initial temperature of 50 °C for 3 minutes, then programmed at 40 °C/min to a temperature of 280 °C, where it was held, post-run, for 2 minutes. The MS detector was at 250 °C, using $H_2$ flow at 40.00 mL/min, air at 400 mL/min and He makeup flow at 45.0 mL/min.

### 2.1 General Procedure A (one amine and one alkyne, homocoupling between amines)

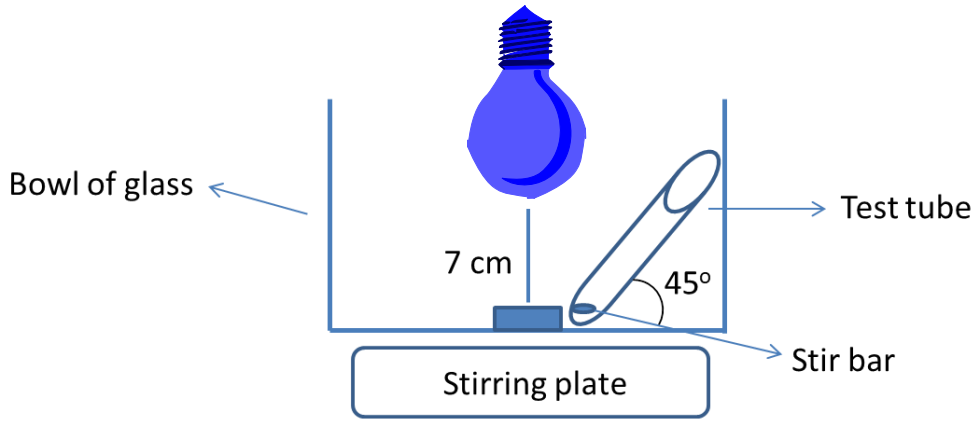
To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), tetrabutylammonium tetrafluoroborate (20 mol%) and NaOH (0.25 mmol, 1 equiv.), aromatic amine (0.50 mmol, 2 equiv.) and alkyne (0.25 mmol, 1 equiv.) were added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40 mm internal diameter, 7.5 g of $SiO_2$) using 55 mL of a mixture of ethyl acetate / n-hexane (10/90) and followed by TLC to afford the desired pure product.

### 2.2 General Procedure B (two amines and one alkyne, heterocoupling between amines)

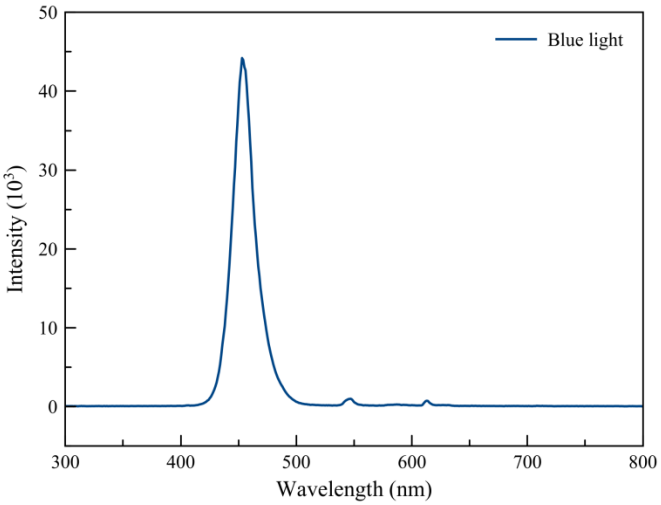
To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), tetrabutylammonium tetrafluoroborate (20 mol%) and NaOH (0.25 mmol, 1 equiv.), aromatic amine (0.75 mmol, 3 equiv.), aliphatic amine or second aromatic amine (0.25 mmol, 1 equiv.) and alkyne (0.25 mmol, 1 equiv.) were added. The reaction mixture

was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40 mm internal diameter, 7.5 g of $SiO_2$) using 55 mL of a mixture of ethyl acetate / n-hexane (10/90) and followed by TLC to afford the desired pure product. For product **3o**, we used 3 equiv. of heptylamine, 1 equiv. of benzylamine and 1 equiv. of phenylacetylene.

A description of the apparatus for the photoreaction is shown below:




The emission spectrum of the blue LED is shown below:




**3. Scheme 3, gram-scale preparation of 3a**

To a solution of 30 mL of water containing $(NH_4)_2S_2O_8$ (10 mmol, 1 equiv), tetrabutylammonium tetrafluoroborate (20 mol%) and NaOH (10 mmol, 1 equiv.), aromatic amine (20 mmol, 2 equiv.) and alkyne (10 mmol, 1 equiv.) were added. The round bottom flask was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40 mm internal diameter, 15 g of SiO2) using 150 mL of a mixture of ethyl acetate / n-hexane (10/90) and followed by TLC to afford product **3a** in 72% yield.

**4. Scheme 4, b in the main text**

To a solution of 1 mL of water containing tetrabutylammonium tetrafluoroborate (20 mol%) and NaOH (0.25 mmol, 1 equiv.), commercial imine **A** (*N*-Benzylidenebenzylamine, 0.25 mmol) and phenylacetylene (0.25 mmol) were added. The reaction mixture was capped with a rubber septum and stirred for 24 h at room temperature. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. After the extraction, the crude mixture was diluted with ethyl acetate, filtered and analysed by GC-MS (Figure S1).

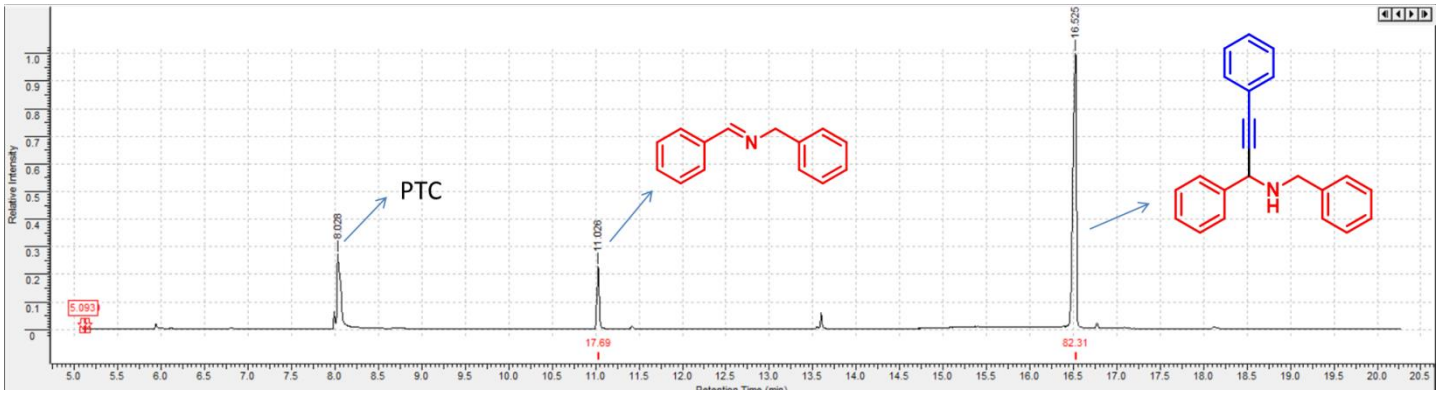



**Figure S1.** GC-MS of the reaction displayed in Scheme 4, b in the main text.

**5. Scheme 4, c in the main text**

To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), benzylamine (0.50 mmol, 2 equiv.) was added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. After the extraction, the crude mixture was diluted with ethyl acetate, filtered and analysed by GC-MS (Figure S2).

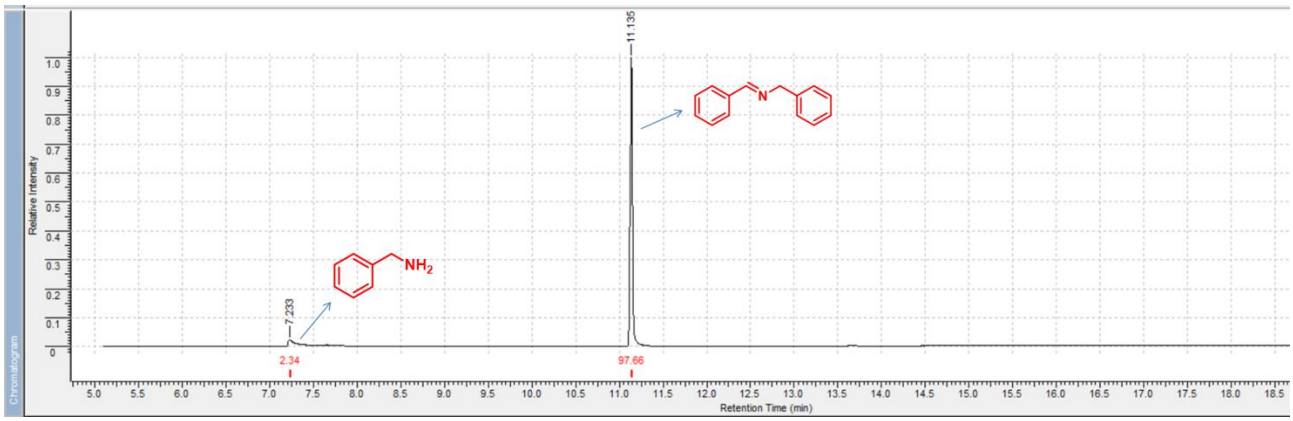



**Figure S2.** GC-MS of the reaction displayed in Scheme 4, c in the main text.

**6. Scheme 4, d in the main text**

To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), benzylamine (0.50 mmol, 2 equiv.) and TEMPO (0.50 mmol, 2 equiv.) were added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic

layers were concentrated. After the extraction, the crude mixture was diluted with ethyl acetate, filtered and analysed by GC-MS (Figure S3).

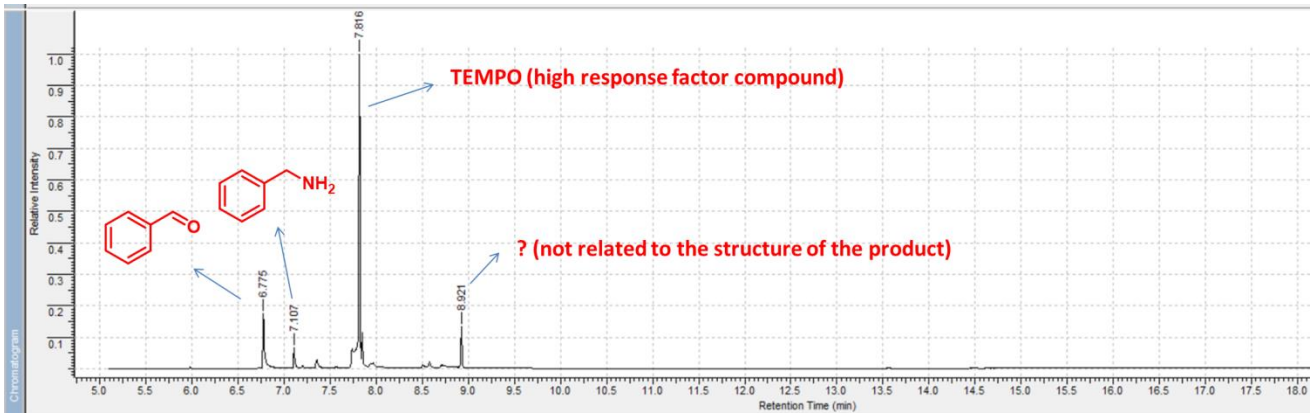



**Figure S3.** GC-MS of the reaction displayed in Scheme 4, d in the main text.

## 7. Scheme 4, e in the main text

To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), benzylamine (0.50 mmol, 2 equiv.) and 2-propanol (0.50 mmol, 2 equiv.) were added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. After the extraction, the crude mixture was diluted with ethyl acetate, filtered and analysed by GC-MS (Figure S4).

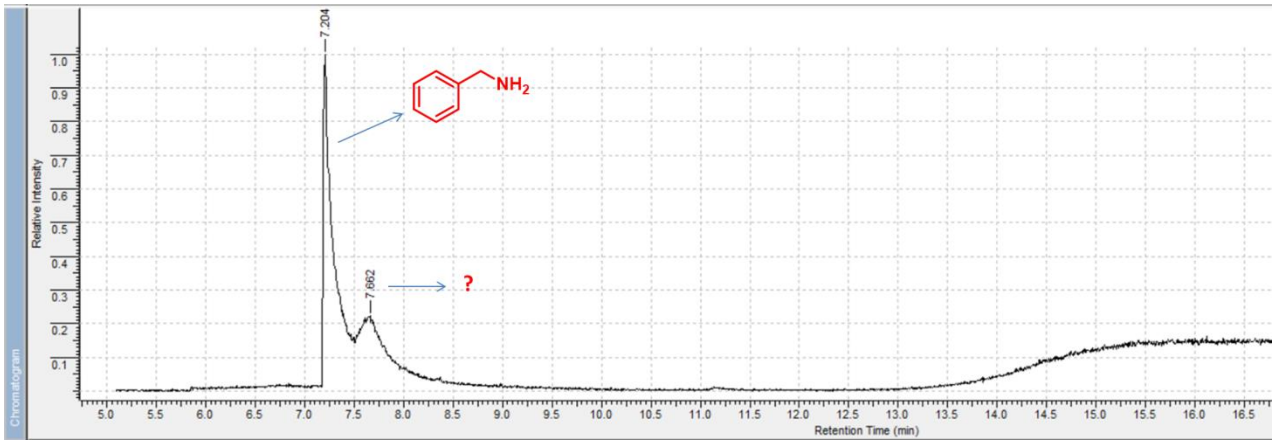



**Figure S4.** GC-MS of the reaction displayed in Scheme 4, e in the main text.

## 8. Scheme 4, f in the main text

To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), benzylamine (0.50 mmol, 2 equiv.) and tert-butanol (0.50 mmol, 2 equiv.) were added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. After the extraction, the crude mixture was diluted with ethyl acetate, filtered and analysed by GC-MS (Figure S5).

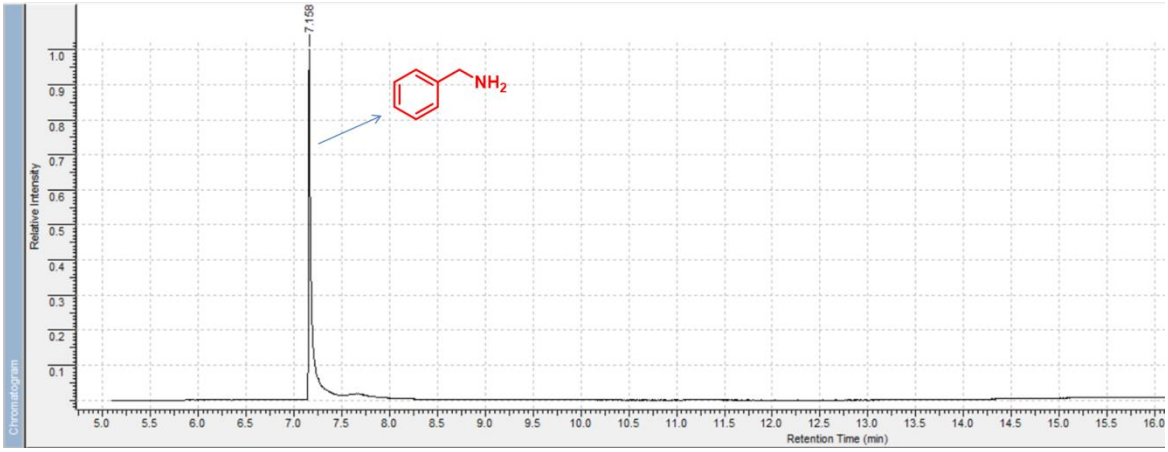



**Figure S5.** GC-MS of the reaction displayed in Scheme 4, f in the main text.

## 9. Scheme 4, g in the main text

To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), benzylamine (0.50 mmol, 2 equiv.) and $CuCl_2$ (0.25 mmol, 1 equiv.) were added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40 mm internal diameter, 7.5 g of $SiO_2$) using 55 mL of a mixture of ethyl acetate / n-hexane (10/90) and followed by TLC to afford the desired product in 26% yield.

## 10. Scheme 4, h in the main text

To a solution of 1 mL of water containing $(NH_4)_2S_2O_8$ (0.25 mmol, 1 equiv), benzylamine (0.50 mmol, 2 equiv.) and BHT (0.25 mmol, 1 equiv.) were added. The reaction mixture was capped with a rubber septum and irradiated using blue LED (15 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40

mm internal diameter, 7.5 g of $SiO_2$) using 55 mL of a mixture of ethyl acetate / n-hexane (10/90) and followed by TLC to afford the desired product in 39% yield.

## 11. Scheme 4, i in the main text

To a solution of 1 mL of water containing NaOH (0.25 mmol, 1 equiv.), commercial imine **A** (*N*-Benzylidenebenzylamine, 0.25 mmol) and phenylacetylene (0.25 mmol) were added. The reaction mixture was capped with a rubber septum and stirred for 24 h at room temperature. Then, the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. After the extraction, the crude mixture was diluted with ethyl acetate, filtered and analysed by GC-MS (Figure S6).

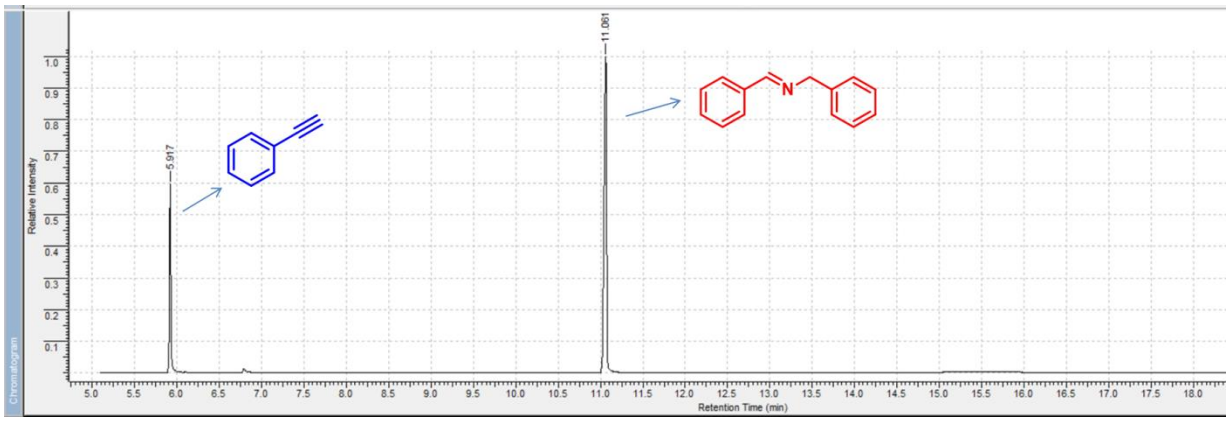
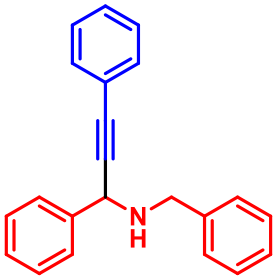



**Figure S6.** GC-MS of the reaction displayed in Scheme 4, i in the main text.

## 12. Characterization of the products

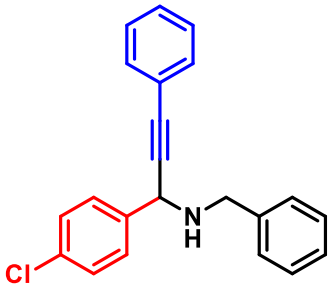



**3a**

Prepared from benzylamine and phenylacetylene following the general procedure A to give the product as colourless oil (82% yield). All data was consistent with that previously reported.[1]

[1] H. Li, H. Feng, J. Zhang, E. V. Van Der Eycken and L. Huang, *J. Org. Chem.*, 2019, **84**, 10501–10508.

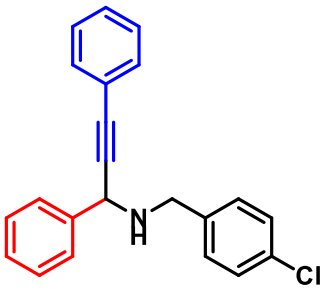
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.74 (d, 2H, $J$ = 7.34 Hz), 7.62–7.60 (m, 2H), 7.53–7.34 (m, 11H), 4.92 (s, 1H), 4.12 (d, 1H, $J$ = 13.2 Hz), 4.09 (d, 1H, $J$ = 13.2 Hz), 2.00 (bs, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.24, 139.72, 131.66, 128.41, 128.34, 128.21, 128.09, 127.67, 127.57, 126.99, 123.07, 89.17, 85.67, 53.56, 51.05.




**3b**

Prepared from 4-chlorobenzylamine (3 equiv.), benzylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as colourless oil (72% yield). All data was consistent with that previously reported.[2]

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.63 (d, 2H, $J$ = 10.76 Hz), 7.58–7.56 (m, 2H), 7.47 (d, 2H, $J$ = 6.85 Hz), 7.43–7.38 (m, 7H), 7.33 (t, 1H, $J$ = 6,36 Hz), 4.85 (s, 1H), 4.07 (d, 1H, $J$ = 13.20 Hz), 4.02 (d, 1H, $J$ = 13.20 Hz), 1.92 (bs, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 139.54, 138.79, 133.43, 131.68, 128.51, 128.40, 128.34, 128.28, 127.11, 122.84, 88.60, 86.03, 52.91, 50.98.



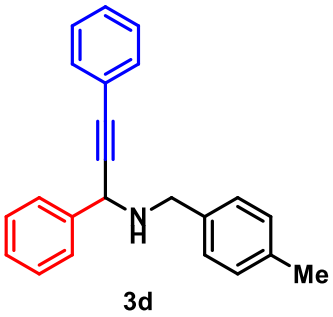

**3c**

Prepared from benzylamine (3 equiv.), 4-chlorobenzylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as colourless oil (69% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.69 (d, 2H, $J$ = 7.83 Hz), 7.59–7.56 (m, 2H), 7.47–7.36 (m, 10H), 4.86 (s, 1H), 4,03 (s, 2H), 1.94 (bs, 1H).

[2] P. K. Mishra, S. Verma, M. Kumar and A. K. Verma, *Org. Lett.*, 2018, **20**, 7182–7185.

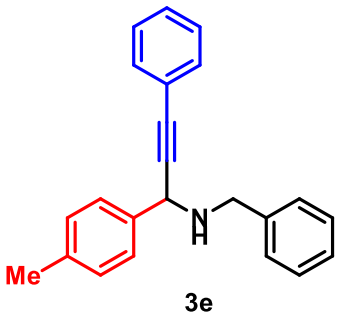
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.06, 138.25, 132.65, 131.65, 129.67, 128.44, 128.42, 128.24, 128.17, 127.75, 122.95, 88.92, 85.84, 53.51, 50.29.
**HRMS** m/z (ESI): calcd. for $C_{22}H_{19}ClN$ $[M+H]^+$ 332.12005, found 332.12054.




**3d**

Prepared from benzylamine (3 equiv.), 4-methylbenzylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as colourless oil (68% yield). All data was consistent with that previously reported.[3]

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.69 (d, 2H, $J$ = 7.53 Hz), 7.57–7.56 (m, 2H), 7.45–7.43 (t, 2H, $J$ = 7.53 Hz), 7.39–7.36 (m, 6H), 7.22–7.21 (d, 2H, $J$ = 8.28 Hz), 4.87 (s, 1H), 4.05–4.03 (d, 1H, $J$ = 12.81 Hz), 4.03–4.01 (d, 1H, $J$ = 12.81 Hz), 2.41(s, 1H), 1.88 (bs, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.34, 136.67, 136.58, 131.69, 129.05, 128.43, 128.35, 128.22, 128.09, 127.67, 127.61, 123.14, 89.26, 85.63, 53.50, 50.81, 21.06.



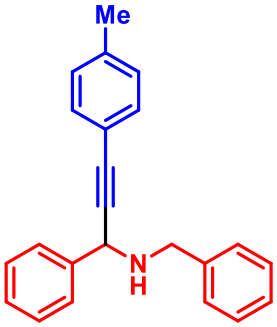

**3e**

Prepared from 4-methylbenzylamine (3 equiv.), benzylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (65% yield). All data was consistent with that previously reported.[3]

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.57–7.54 (m, 4H), 7.48–7.46 (m, 2H), 7.41–7.36 (m, 6H), 7.25–7.24 (d, 2H, $J$ = 6.60 Hz), 4.84 (s, 1H), 4.05 (s, 2H), 2.41(s, 1H), 1.89 (bs, 1H).

[3] A. Casnati, A. Perrone, P. P. Mazzeo, A. Bacchi, R. Mancuso, B. Gabriele, R. Maggi, G. Maestri, E. Motti, A. Stirling and N. Della Ca, *J. Org. Chem.*, 2019, **84**, 3477–3490.

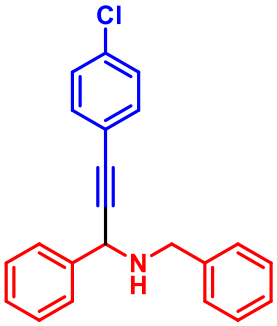
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 139.82, 137.38, 131.69, 129.14, 128.45, 128.38, 128.23, 128.07, 127.72, 127.61, 127.50, 127.00, 123.18, 89.41, 85.46, 53.59, 53.34, 51.05, 21.09.




**3f**

Prepared from benzylamine and 4-methylphenylacetylene following the general procedure A to give the product as colourless oil (83% yield). All data was consistent with that previously reported.[1]

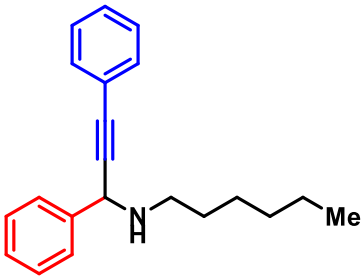
**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.56–7.54 (m, 2H), 7.36–7.30 (m, 6H), 7.29–7.28 (m, 1H), 7.25–7.18 (m, 3H), 7.08–7.06 (d, 2H, $J$ = 7.86 Hz), 4.74 (s, 1H), 3.96–3.93 (d, 1H, $J$ = 12.89 Hz), 3.93–3.90 (d, 1H, $J$ = 13.20 Hz), 2.29 (s, 3H), 1.70 (bs, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.39, 139.78, 138.23, 131.61, 129.02, 128.43, 128.39, 127.65, 127.04, 88.38, 85.83, 53.63, 51.09, 21.44.




**3g**

Prepared from benzylamine and 4-chlorophenylacetylene following the general procedure A to give the product as colourless oil (80% yield). All data was consistent with that previously reported.[1]

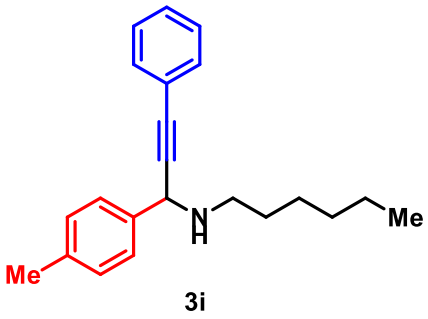
**$^{1}$H NMR** (500 MHz, $CDCl_3$): 7.53–7.52 (m, 2H), 7.35–7.28 (m, 7H), 7.26–7.18 (m, 5H), 4.73 (s, 1H), 3.94–3.92 (d, 1H, $J$ = 13.20 Hz), 3.91–3.88 (d, 1H, $J$ = 13.20 Hz), 1.75 (bs, 1H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.04, 139.61, 134.17, 132.95, 128.59, 128.43, 128.38, 127.59, 127.12, 121.57, 90.21, 84.55, 53.61, 51.12.




**3h**

Prepared from benzylamine (3 equiv.), hexylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (75% yield). All data was consistent with that previously reported.[4]

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.62–7.60 (m, 2H), 7.50–7.47 (m, 2H), 7.41–7.37 (m, 2H), 7.33–7.31 (m, 4H), 4.82 (s, 1H), 2.89–2.83 (m, 1H), 2.77–2.70 (m, 1H), 1.60–1.52 (m, 2H), 1.38–1.29 (m, 6H), 0.89 (t, 3H, $J$ = 6.85 Hz).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 131.69, 128.49, 128.22, 128.08, 127.69, 127.60, 54.69, 47.36, 31.73, 29.89, 27.03, 22.60, 14.04.

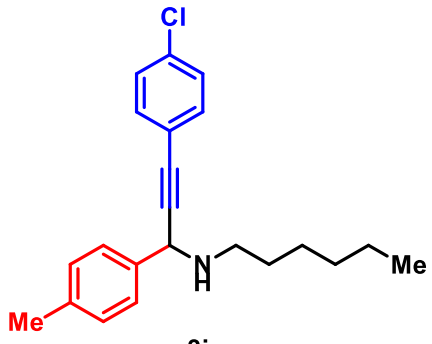



**3i**

Prepared from 4-methylbenzylamine (3 equiv.), hexylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (77% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.50–7.47 (m, 4H), 7.32–7.31 (m, 3H), 7.21–7.19 (d, 2H, $J$ = 7.86 Hz), 4.80 (s, 1H), 2.87–2.82 (m, 1H), 2.76–2.71 (m, 1H), 2.37 (s, 3H), 1.59–1.53 (m, 2H), 1.37–1.28 (m, 6H), 0.91–0.88 (t, 3H, $J$ = 6.92 Hz).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 137.43, 131.69, 129.17, 128.19, 128.05, 127.53, 123.18, 54.37, 47.23, 31.72, 29.77, 27.02, 22.59, 21.10, 14.03.
**HRMS** m/z (ESI): calcd. for C22H28N $[M+H]^+$ 306.22163, found 306.22145.

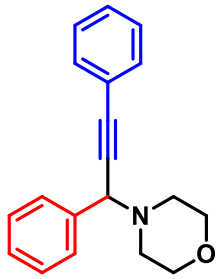
[4] H. Feng, D. S. Ermolat'Ev, G. Song and E. V. Van Der Eycken, *J. Org. Chem.*, 2011, **76**, 7608–7613.




3j

Prepared from 4-methylbenzylamine (3 equiv.), hexylamine (1 equiv.) and 4-chlorophenylacetylene following the general procedure B to give the product as colourless oil (73% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.47–7.45 (d, 2H, $J$ = 7.86 Hz), 7.41–7.38 (dt, 2H, $J$ = 8.80; 2.20), 7.30–7.27 (dt, 2H, $J$ = 8.49; 1.89 Hz), 7.20–7.19 (d, 2H, $J$ = 7.86 Hz), 4.77 (s, 1H), 2.85–2.80 (m, 1H), 2.73–2.68 (m, 1H), 2.37 (s, 3H), 1.65 (bs, 1H), 1.58–1.51 (m, 2H), 1.38–1.27 (m, 6H), 0.91–0.88 (t, 3H, $J$ = 6.60 Hz).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 137.48, 137.36, 134.02, 132.90, 129.21, 128.52, 127.41, 121.71, 90.77, 83.90, 54.43, 47.37, 31.72, 29.89, 27.02, 22.59, 21.10, 14.03.
**HRMS** m/z (ESI): calcd. For $C_{22}H_{27}ClN$ $[M+H]^+$ 340.18265, found 340.18288.

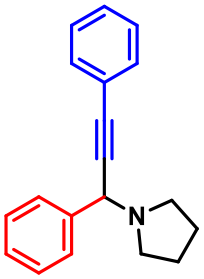



3k

Prepared from benzylamine (3 equiv.), morpholine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (68% yield). All data was consistent with that previously reported.[5]

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.69–7.67 (m, 2H), 7.42–7.39 (m, 2H), 7.37–7.33 (m, 4H), 4.83 (s, 1H), 3.81–3.74 (m, 4H), 2.70–2.65 (m, 4H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 137.68, 131.74, 128.53, 128.17, 127.72, 122.89, 88.46, 84.94, 67.06, 61.97, 49.80.

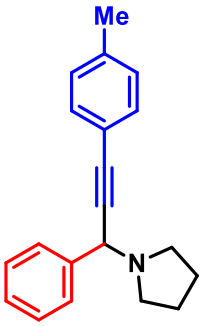
[5] L. Shi, Y. Q. Tu, M. Wang, F. M. Zhang and C. A. Fan, *Org. Lett.*, 2004, **6**, 1001–1003.



**3l**

Prepared from benzylamine (3 equiv.), pyrrolidine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (78% yield). All data was consistent with that previously reported.[6]

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.65–7.62 (m, 2H), 7.52–7.49 (m, 2H), 7.41–7.31 (m, 6H), 4.93 (s, 1H), 2.76–3.71 (m, 4H), 1.85–1.81 (m, 4H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 139.14, 131.77, 128.31, 128.25, 128.12, 127.65, 123.11, 87.07, 86.37, 59.11, 50.27, 23.48.

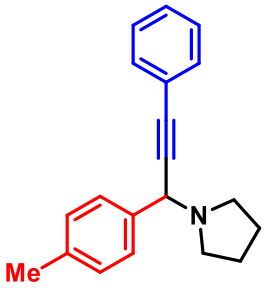


**3m**

Prepared from benzylamine (3 equiv.), pyrrolidine (1 equiv.) and 4-methylphenylacetylene following the general procedure B to give the product as colourless oil (77% yield).

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.68–7.67 (m, 2H), 7.46–7.40 (m, 4H), 7.35–7.32 (tt, 1H, $J$ = 7.23 Hz; 2.20 Hz), 7.18–7.16 (d, 2H, $J$ = 7.86 Hz), 4.94 (s, 1H), 2.77–2.74 (m, 4H), 2.39 (s, 3H), 1.87–1.84 (m, 4H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 139.55, 138.01, 131.57, 128.91, 128.19, 128.13, 127.42, 120.08, 86.92, 85.82, 59.05, 50.16, 23.41, 21.35.
**HRMS** m/z (ESI): calcd. For C20H22N $[M+H]^+$ 276.17468, found 276.17452.

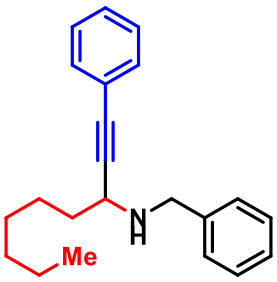
[6] C. Wei, Z. Li and C.-J. Li, *Org. Lett.*, 2003, **5**, 4473–4475.




**3n**

Prepared from 4-methylbenzylamine (3 equiv.), pyrrolidine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (76% yield). All data was consistent with that previously reported.[7]

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.52–7.49 (m, 4H), 7.34–7.32 (m, 3H), 7.20–7.18 (d, 2H, $J$ = 7.86 Hz), 4.90 (s, 1H), 2.75–2.73 (m, 4H), 2.37 (s, 3H), 1.84–1.82 (m, 4H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 137.32, 131.74, 128.93, 128.22, 128.05, 123.16, 86.78, 86.65, 58.82, 50.24, 23.44, 21.09.

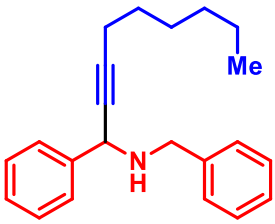



**3o**

Prepared from heptylamine (3 equiv.), benzylamine (1 equiv.) and phenylacetylene following the general procedure B to give the product as pale yellow oil (59% yield). All data was consistent with that previously reported.

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.49–7.47 (m, 2H), 7.43–7.42 (d, 2H, $J$ = 7.53 Hz), 7.37–7.33 (m, 5H), 7.30–7.28 (d, 1H, $J$ = 6.78 Hz), 4.14–4.11 (d, 1H, $J$ = 12.8 Hz), 3.94–3.92 (d, 1H, $J$ = 12.8 Hz), 3.63–3.61 (dd, 1H, $J$ = 7.53 Hz; 6.02 Hz), 1.91 (bs, 1H), 1.81–1.71 (m, 2H), 1.60–1.50 (m, 2H), 1.38–1.29 (m, 6H), 0.92–0.90 (t, 3H, $J$ = 6.78 Hz).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 139.82, 131.66, 128.45, 128.38, 128.22, 127.90, 127.02, 123.39, 90.85, 84.08, 51.43, 50.02, 36.02, 31.73, 29.06, 26.08, 22.58, 14.05.
**HRMS** m/z (ESI): calcd. For C22H28N $[M+H]^+$ 306.22163, found 306.22150.

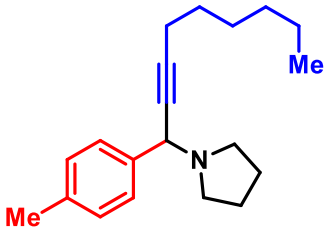
[7] S. Samai, G. C. Nandi and M. S. Singh, *Tetrahedron Lett.*, 2010, **51**, 5555–5558.




**3p**

Prepared from benzylamine and 1-octyne following the general procedure A to give the product as colourless oil (80% yield). All data was consistent with that previously reported.[8]

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.60–7.58 (d, 2H, $J$ = 7.55 Hz), 7.43–7.29 (m, 8H), 4.61 (s, 1H), 3.98–3.96 (d, 1H, $J$ = 12.89 Hz), 3.95–3.92 (d, 1H, $J$ = 12.89 Hz), 2.35–2.32 (td, 2H, $J$ = 7.23 Hz; 1.89 Hz), 1.87 (bs, 1H), 1.64–1.58 (quint, 2H, $J$ = 7.23 Hz), 1.52–1.46 (quint, 2H, $J$ = 7.23), 1.40–1.33 (m, 4H), 0.96–0.94 (m, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.94, 139.91, 128.31, 127.54, 127.47, 126.93, 86.08, 79.73, 53.21, 50.97, 31.31, 28.84, 28.56, 22.55, 18.82, 14.02.

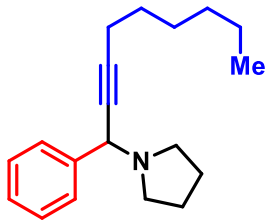



**3q**

Prepared from 4-methylbenzylamine (3 equiv.), pyrrolidine (1 equiv.) and 1-octyne following the general procedure B to give the product as pale yellow oil (75% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.43–7.42 (d, 2H, $J$ = 8.17 Hz), 7.15–7.13 (d, 2H, $J$ = 7.86 Hz), 4.64 (s, 1H), 2.66–2.63 (m, 4H), 2.34 (s, 1H), 2.30–2.27 (td, 2H, $J$ = 7.23 Hz; 1.89 Hz), 1.79–1.77 (quint, 4H, $J$ = 2.83 Hz), 1.58–1.53 (quint, 2H, $J$ = 7.23 Hz), 1.47–1.41 (m, 2H), 1.34–1.30 (m, 4H), 0.92–0.89 (m, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 137.04, 136.58, 128.76, 128.19, 87.06, 76.82, 58.39, 50.04, 31.27, 28.86, 28.51, 23.35, 22.52, 21.03, 18.73, 13.98 .
**HRMS** m/z (ESI): calcd. For C20H30N $[M+H]^+$ 284.23728, found 284.23715.

[8] R. Unnava, M. J. Deka and A. K. Saikia, *Asian J. Org. Chem.*, 2016, **5**, 528–536.

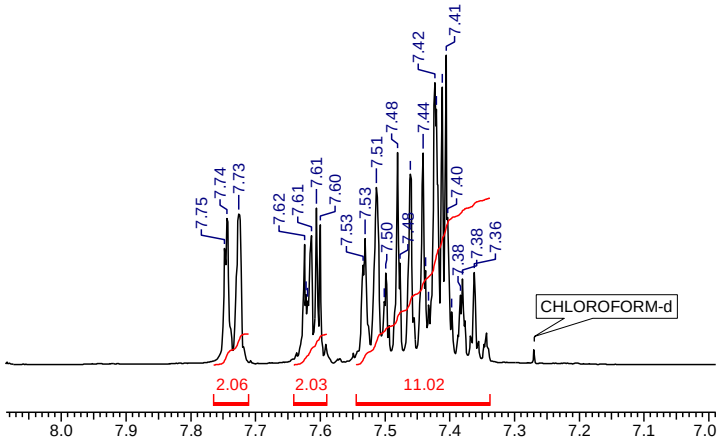



3r

Prepared from benzylamine (3 equiv.), pyrrolidine (1 equiv.) and 1-octyne following the general procedure B to give the product as colourless oil (72% yield).

**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ 7.51–7.49 (d, 2H, $J$ = 7.23 Hz), 7.30–7.27 (m, 2H), 7.24–7.21 (m, 1H), 4.58 (s, 1H), 2.58–2.55 (m, 4H), 2.27–2.23 (td, 2H, $J$ = 7.23 Hz; 2.20 Hz), 1.74–1.72 (m, 4H), 1.54–1.49 (m, 2H), 1.43–1.39 (m, 2H), 1.30–1.25 (m, 4H), 0.88–0.85 (m, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta$ 140.09, 128.18, 128.03, 127.25, 87.03, 76.90, 58.75, 50.11, 31.27, 28.90, 28.51, 23.37, 22.53, 18.73, 13.98.
**HRMS** m/z (ESI): calcd. For C19H28N $[M+H]^+$ 270.22163, found 270.22145.

# 11. Spectral Data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7.44
7.42
7.41
7.40
7.38
7.38
7.36
CHLOROFORM-d
2.06
2.03
11.02
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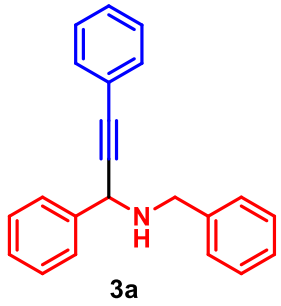
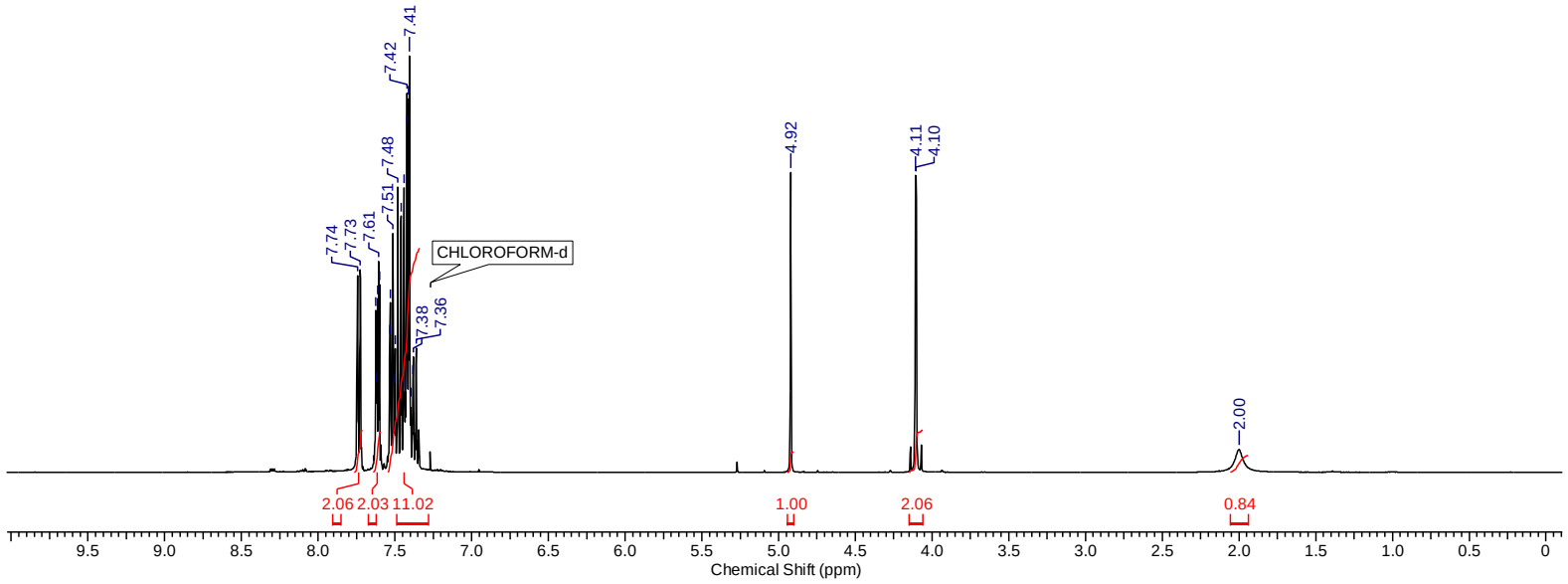
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0


N
H

**3a**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7.36
CHLOROFORM-d
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4.11
4.10
2.00
2.06
2.03
11.02
1.00
2.06
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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1.5
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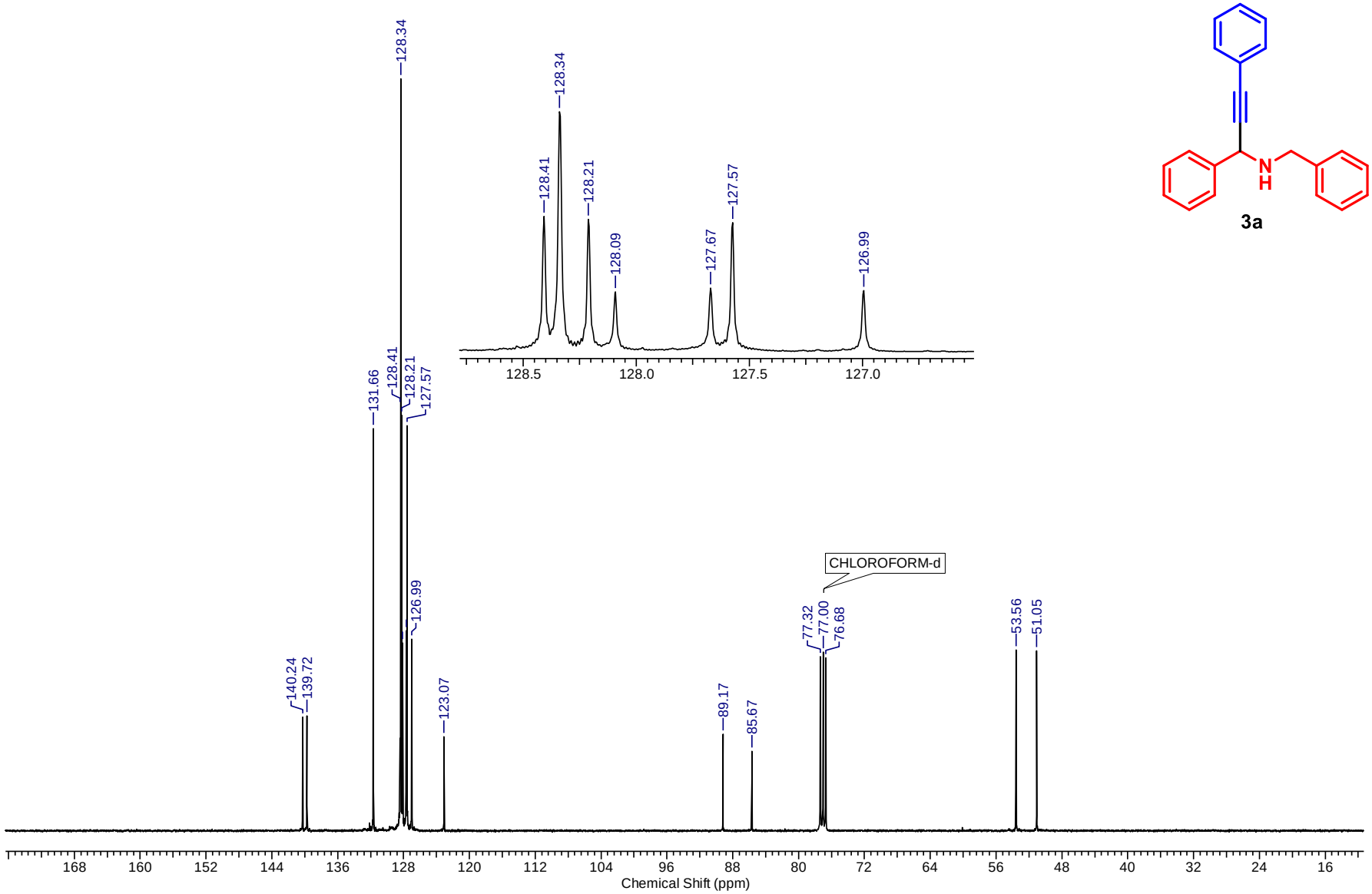
0.5
0
Chemical Shift (ppm)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127.5
127.0
131.66
128.41
128.21
127.57
126.99
140.24
139.72
123.07
89.17
85.67
CHLOROFORM-d
77.32
77.00
76.68
53.56
51.05
168
160
152
144
136
128
120
112
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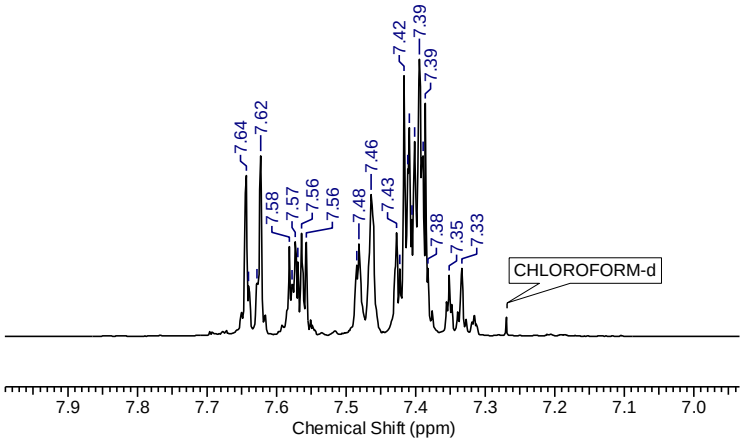
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)
N
H
3a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7.39
7.38
7.35
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CHLOROFORM-d
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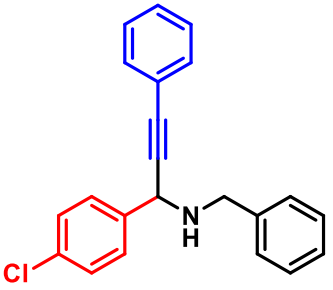
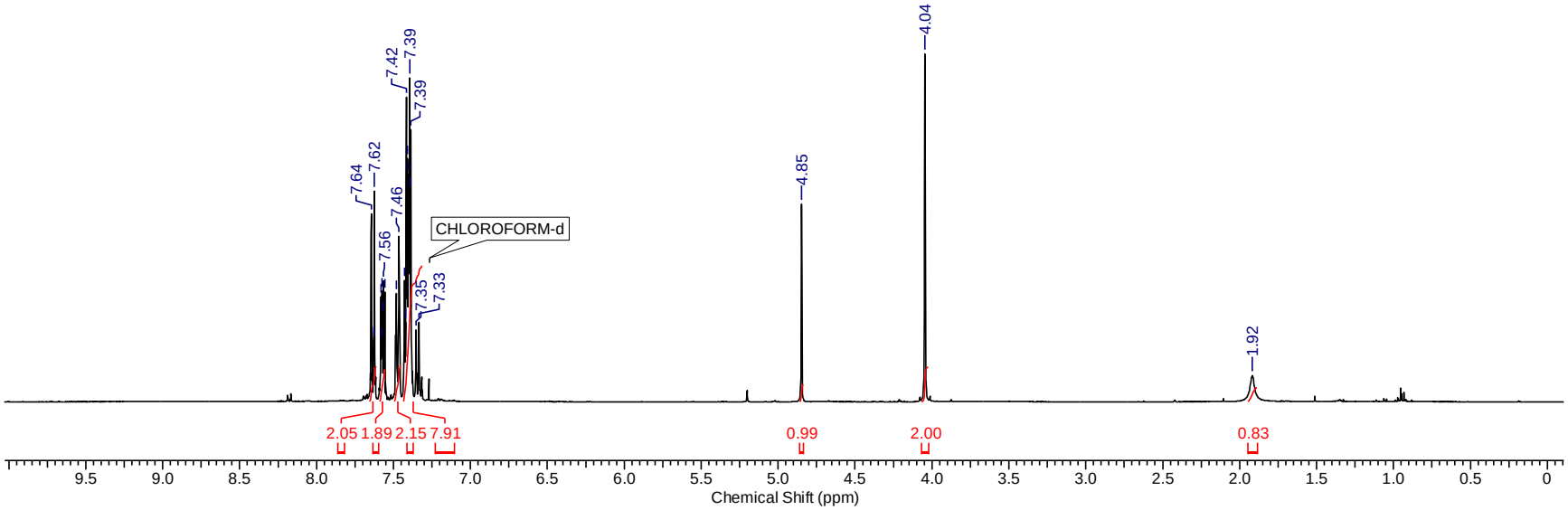
Chemical Shift (ppm)


Cl
N
H

**3b**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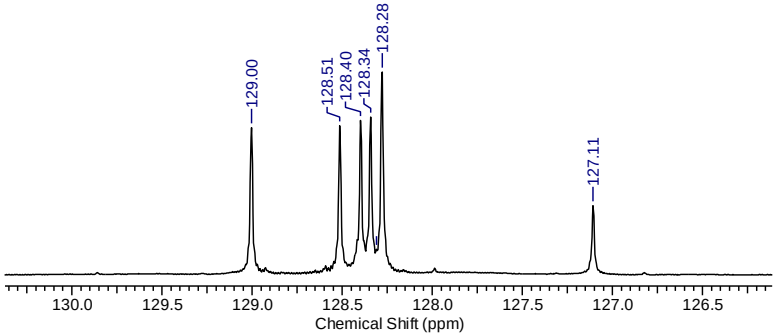
7.62
7.46
7.56
7.35
7.33
7.42
7.39
7.39
CHLOROFORM-d
4.85
4.04
1.92
2.05 1.89 2.15 7.91
0.99
2.00
0.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)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128.0
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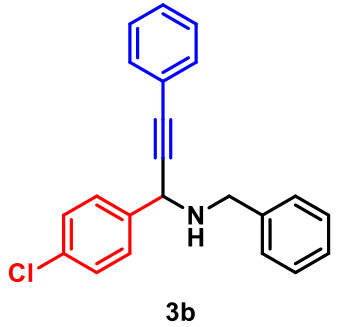
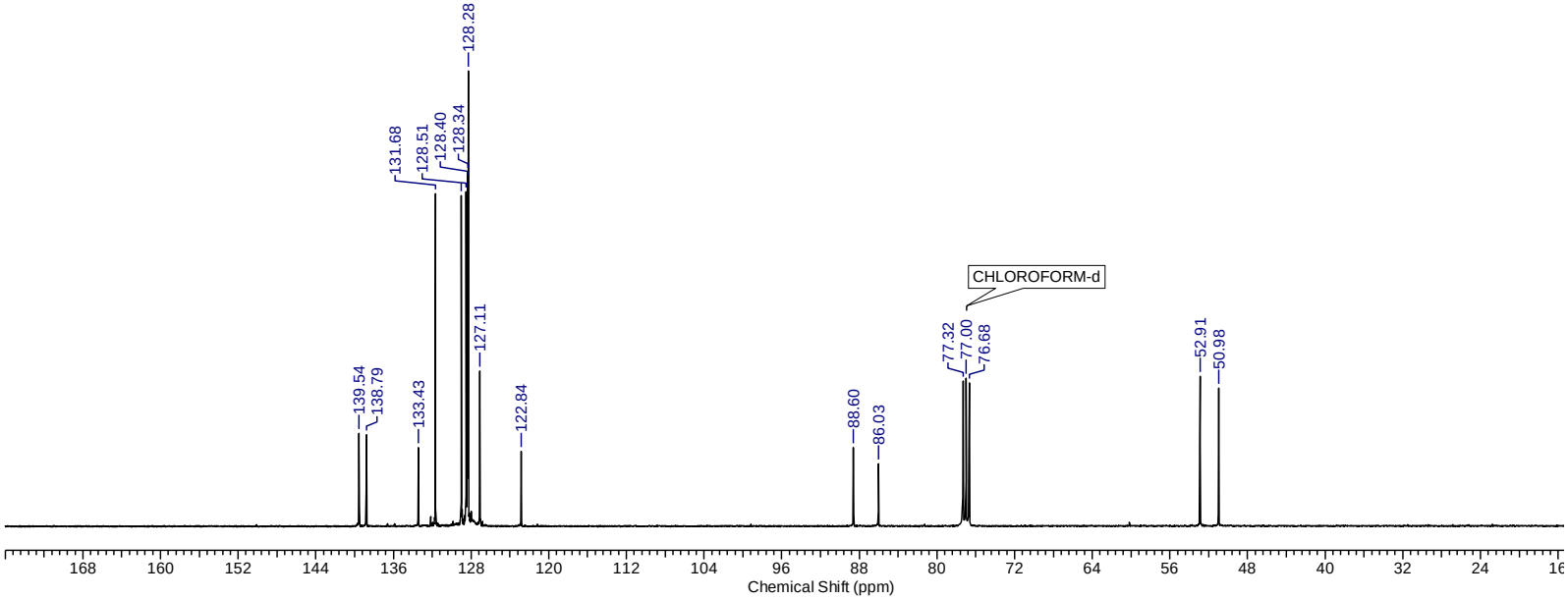
126.5
Chemical Shift (ppm)


Cl
N
H

**3b**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122.84
88.60
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CHLOROFORM-d
77.32
77.00
76.68
52.91
50.98
168
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96
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32
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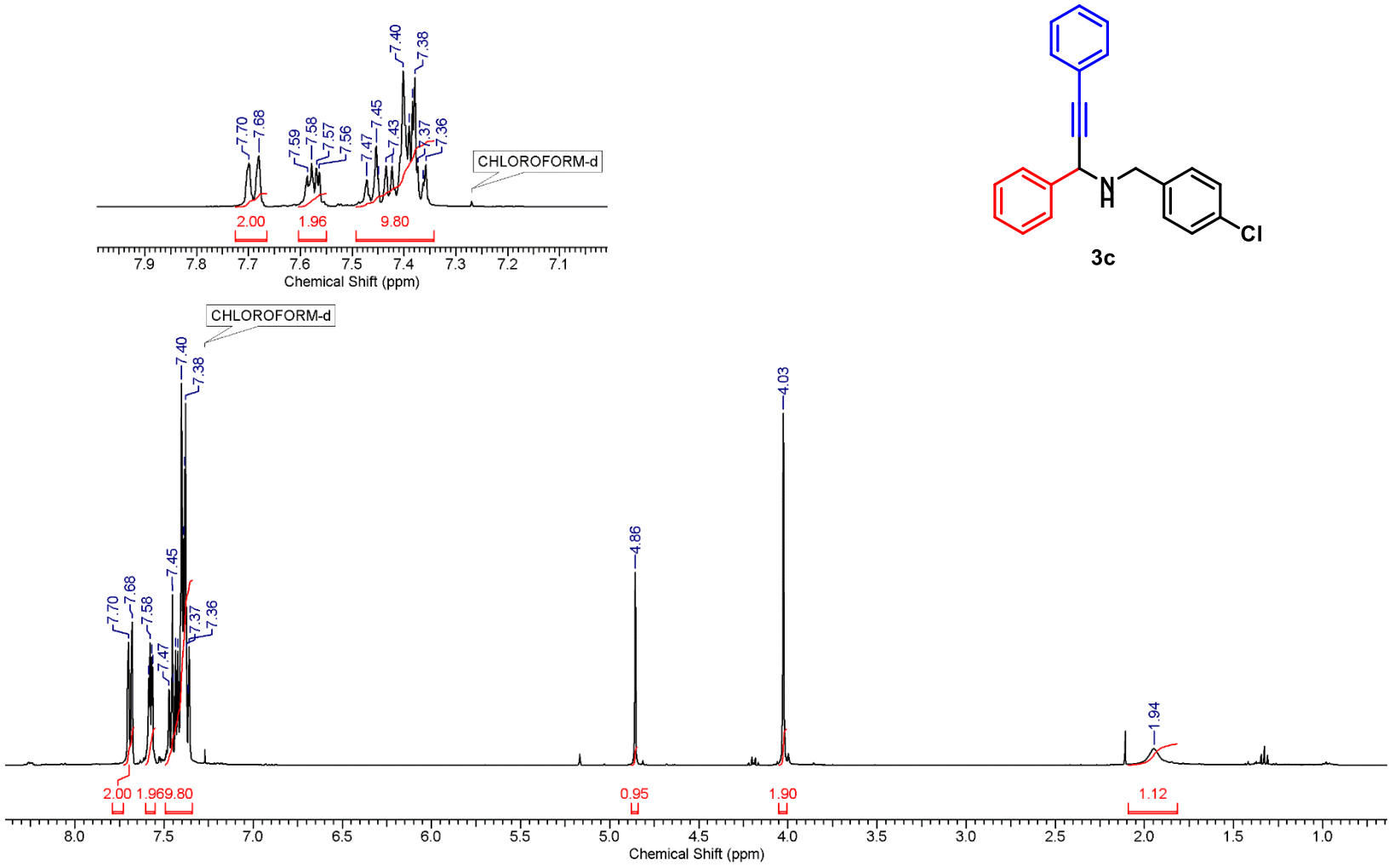
Chemical Shift (ppm)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7.4
7.3
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Chemical Shift (ppm)
CHLOROFORM-d
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1.90
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7.0
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6.0
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5.0
4.5
4.0
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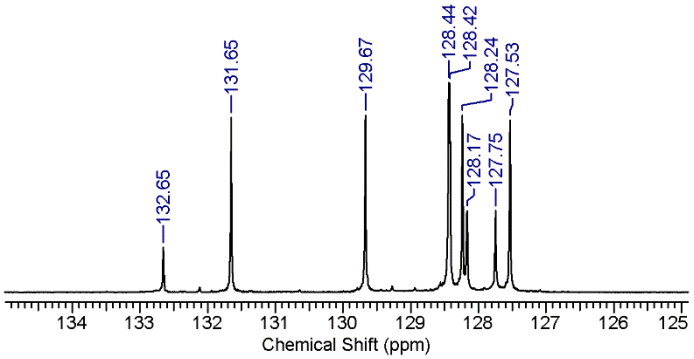
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


N
H
Cl

**3c**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133
132
131
130
129
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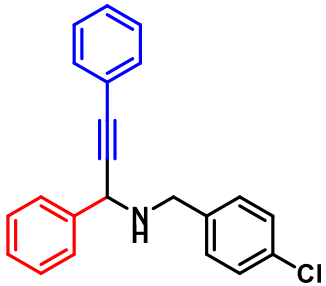
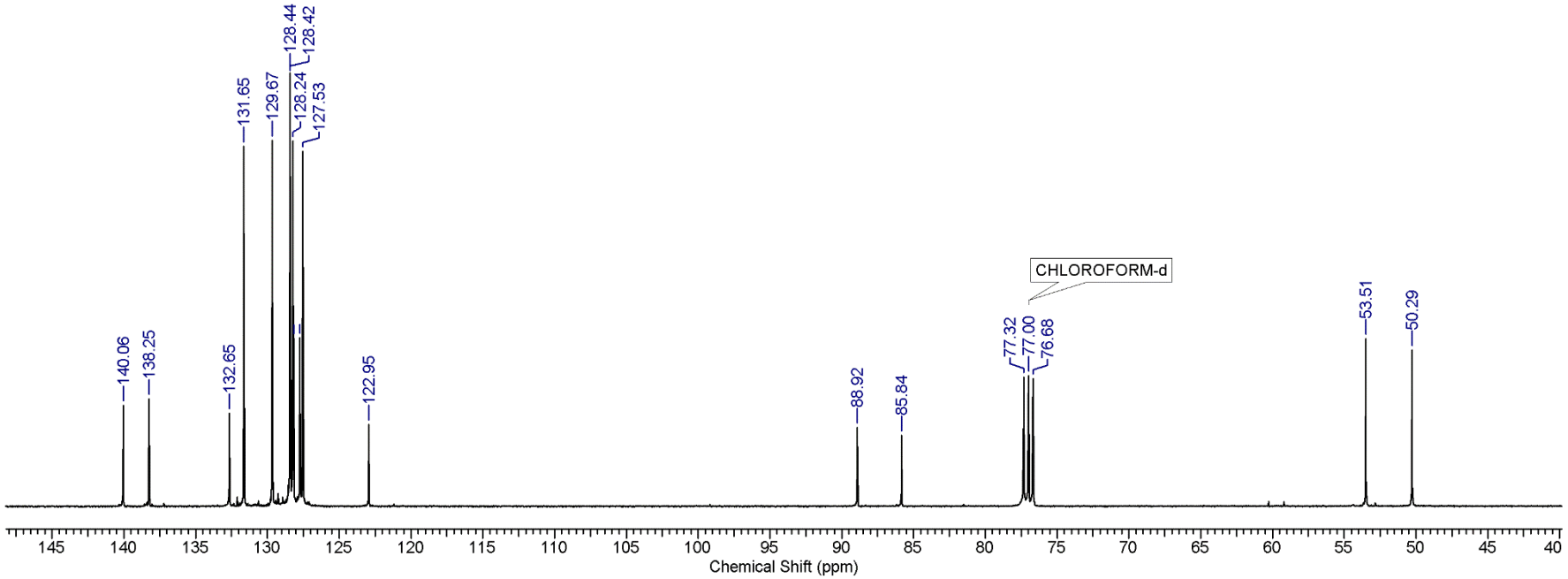
127
126
125
Chemical Shift (ppm)


N
H
Cl

3c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77.32
77.00
76.68
53.51
50.29
145
140
135
130
125
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95
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85
80
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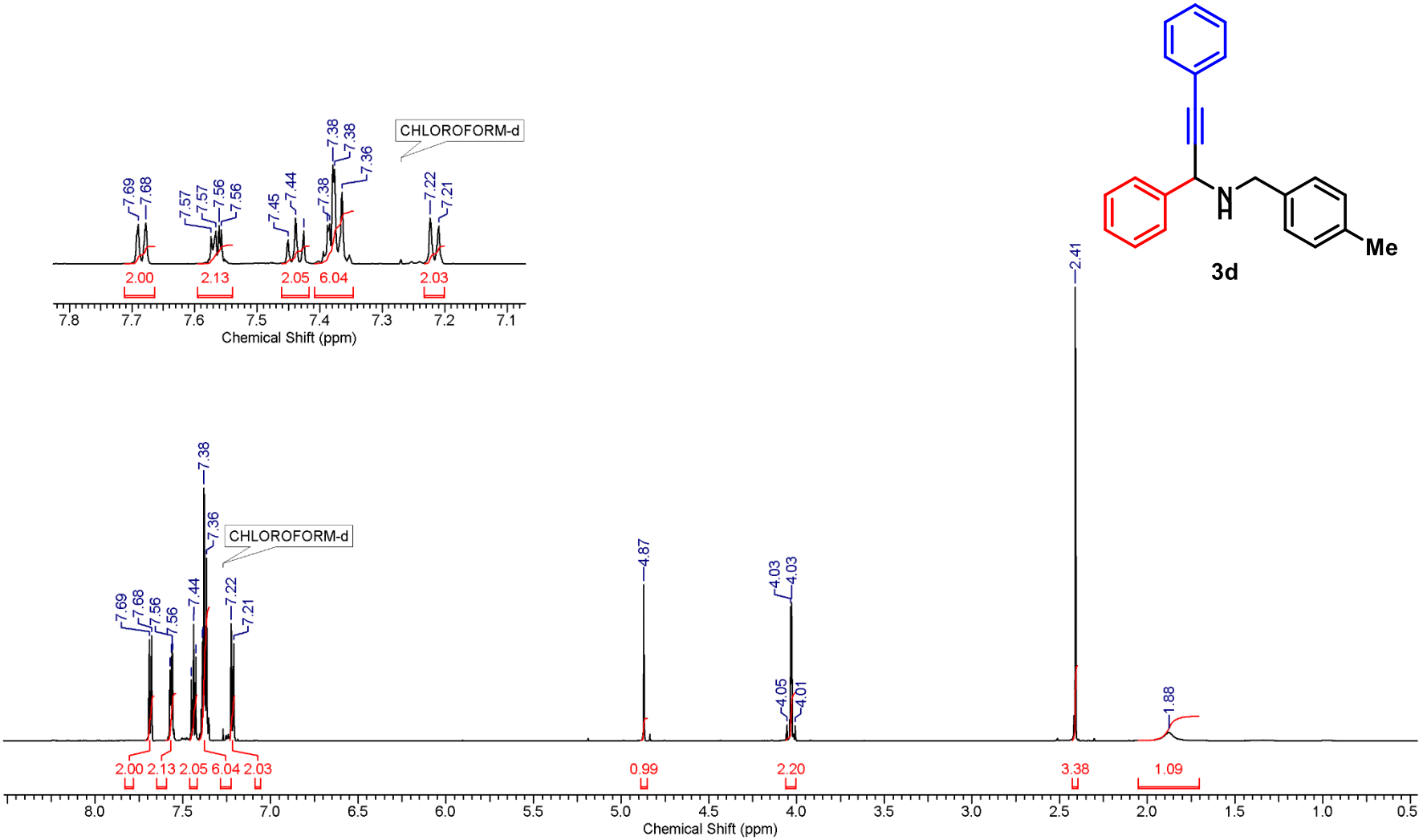
65
60
55
50
45
40
Chemical Shift (ppm)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2.13
2.05
6.04
2.03
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
Me
3d
CHLOROFORM-d
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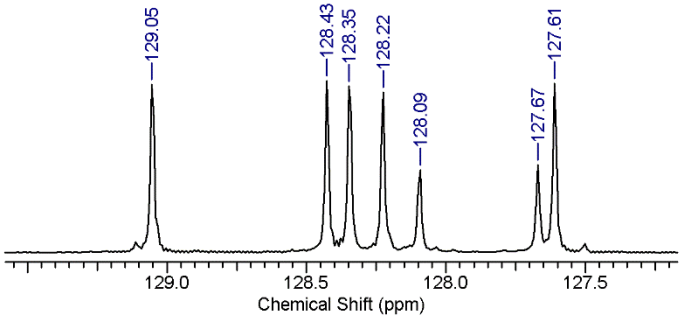
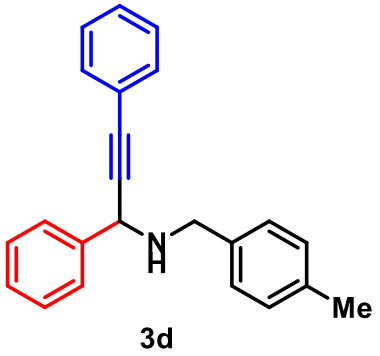
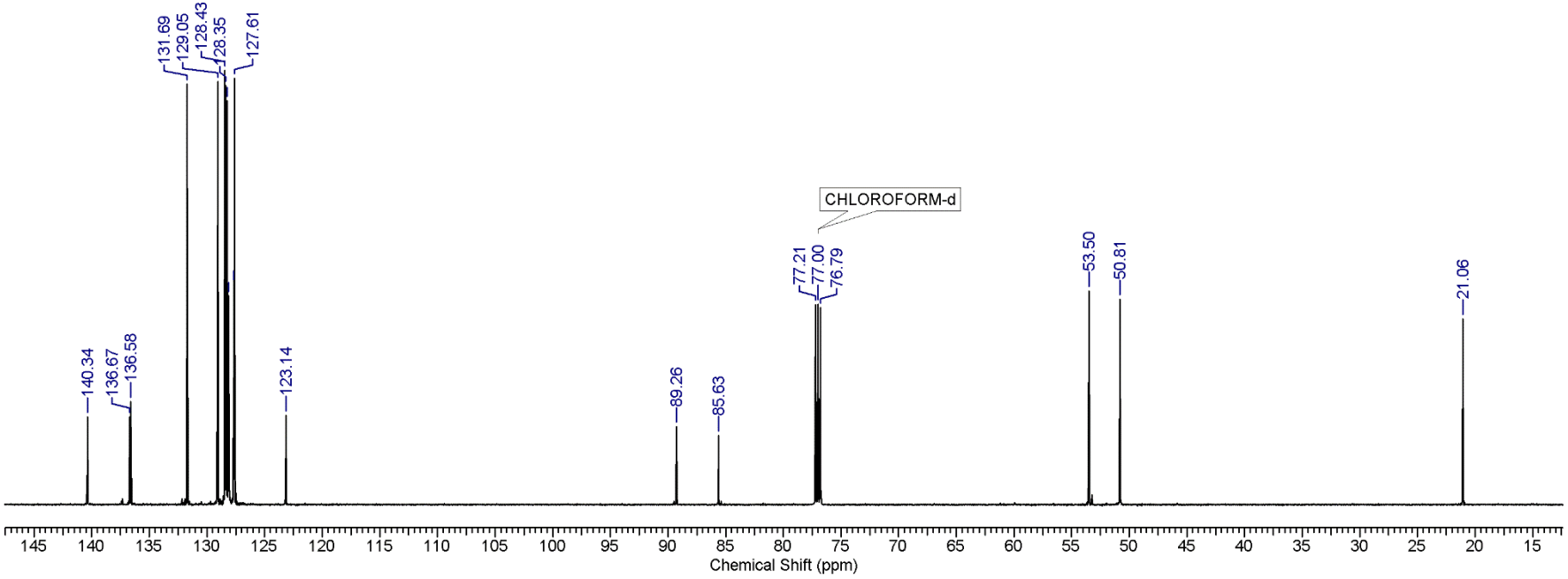
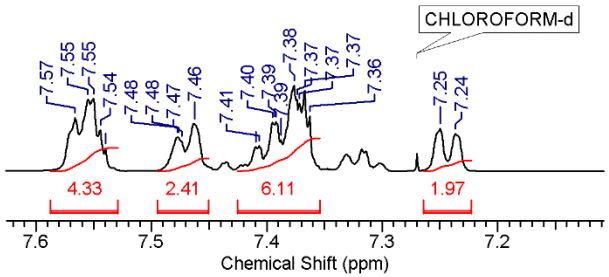
4.03
4.03
4.05
4.01
2.41
1.88
0.99
2.20
3.38
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

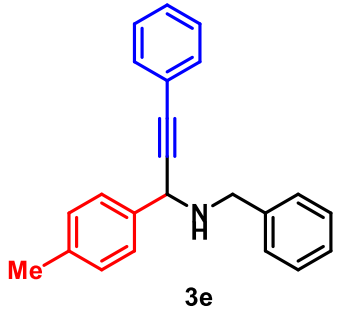

129.05
128.43
128.35
128.22
128.09
127.67
127.61
129.0
128.5
128.0
127.5
Chemical Shift (ppm)


N
H
Me

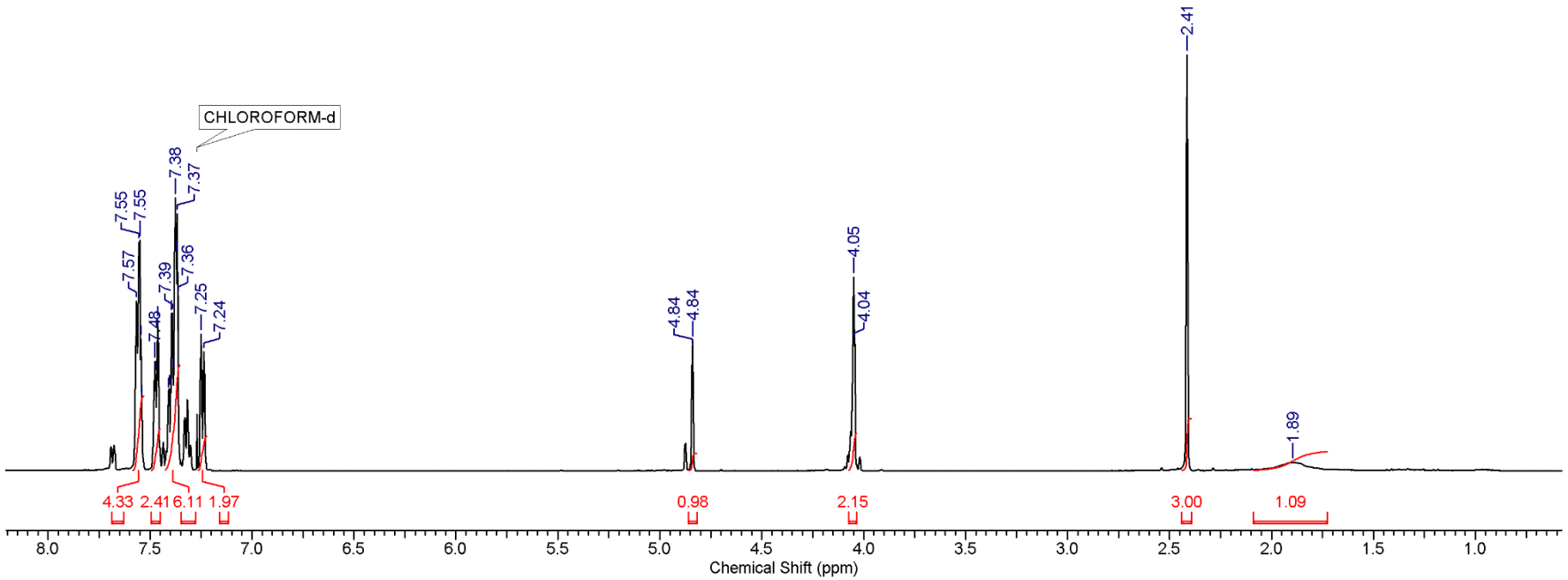
**3d**

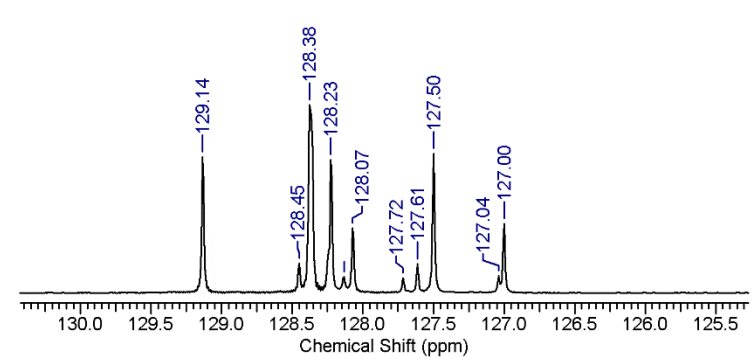

131.69
129.05
128.43
128.35
127.61
140.34
136.67
136.58
123.14
89.26
85.63
CHLOROFORM-d
77.21
77.00
76.79
53.50
50.81
21.06
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
Chemical Shift (ppm)

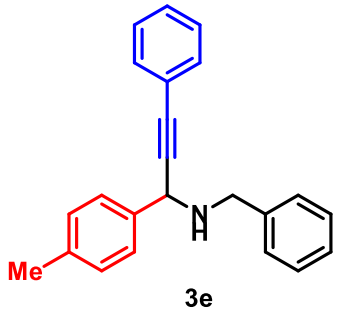

CHLOROFORM-d
7.57
7.55
7.55
7.54
7.48
7.48
7.47
7.46
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.25
7.24
4.33
2.41
6.11
1.97
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)


Me
N
H

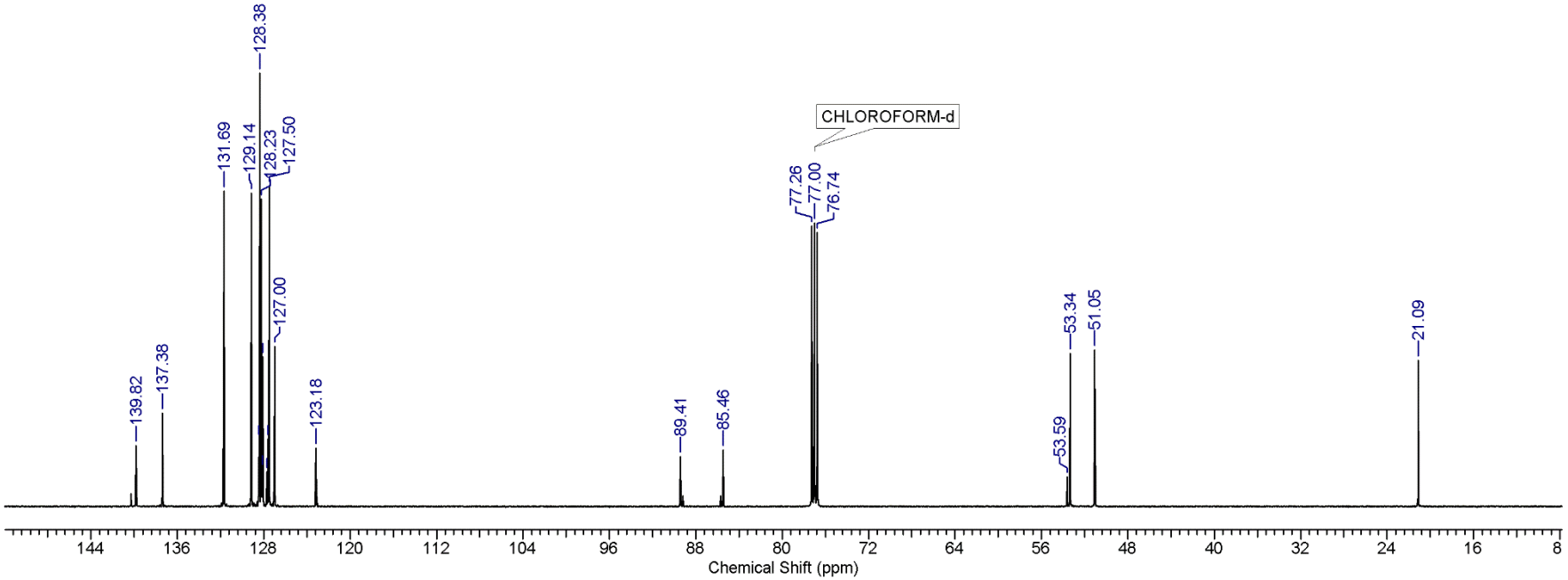
3e

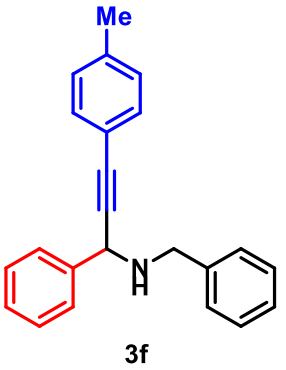

CHLOROFORM-d
7.57
7.55
7.55
7.48
7.39
7.38
7.37
7.36
7.25
7.24
4.84
4.84
4.05
4.04
2.41
1.89
4.33
2.41
6.11
1.97
0.98
2.15
3.00
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


129.14
128.45
128.38
128.23
128.07
127.72
127.61
127.50
127.04
127.00
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
Chemical Shift (ppm)

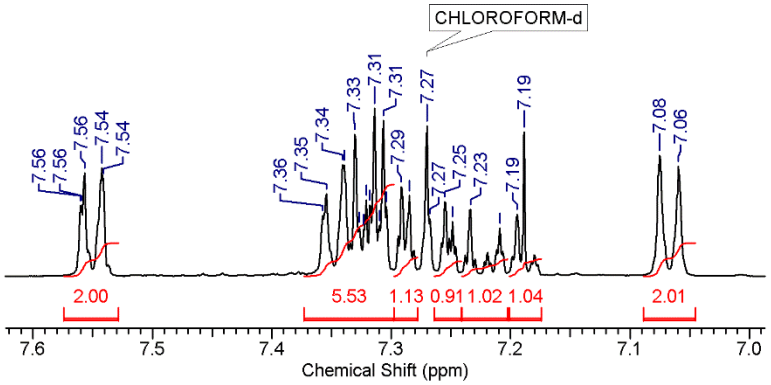

Me
N
H

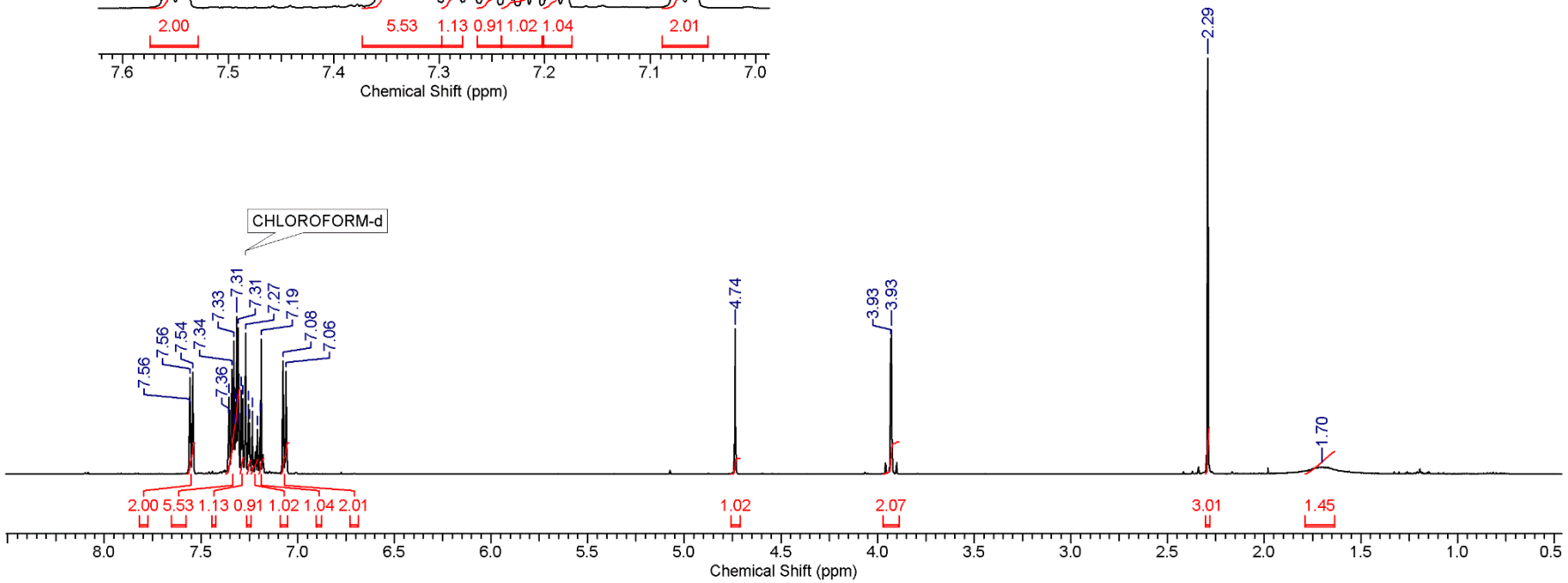
3e

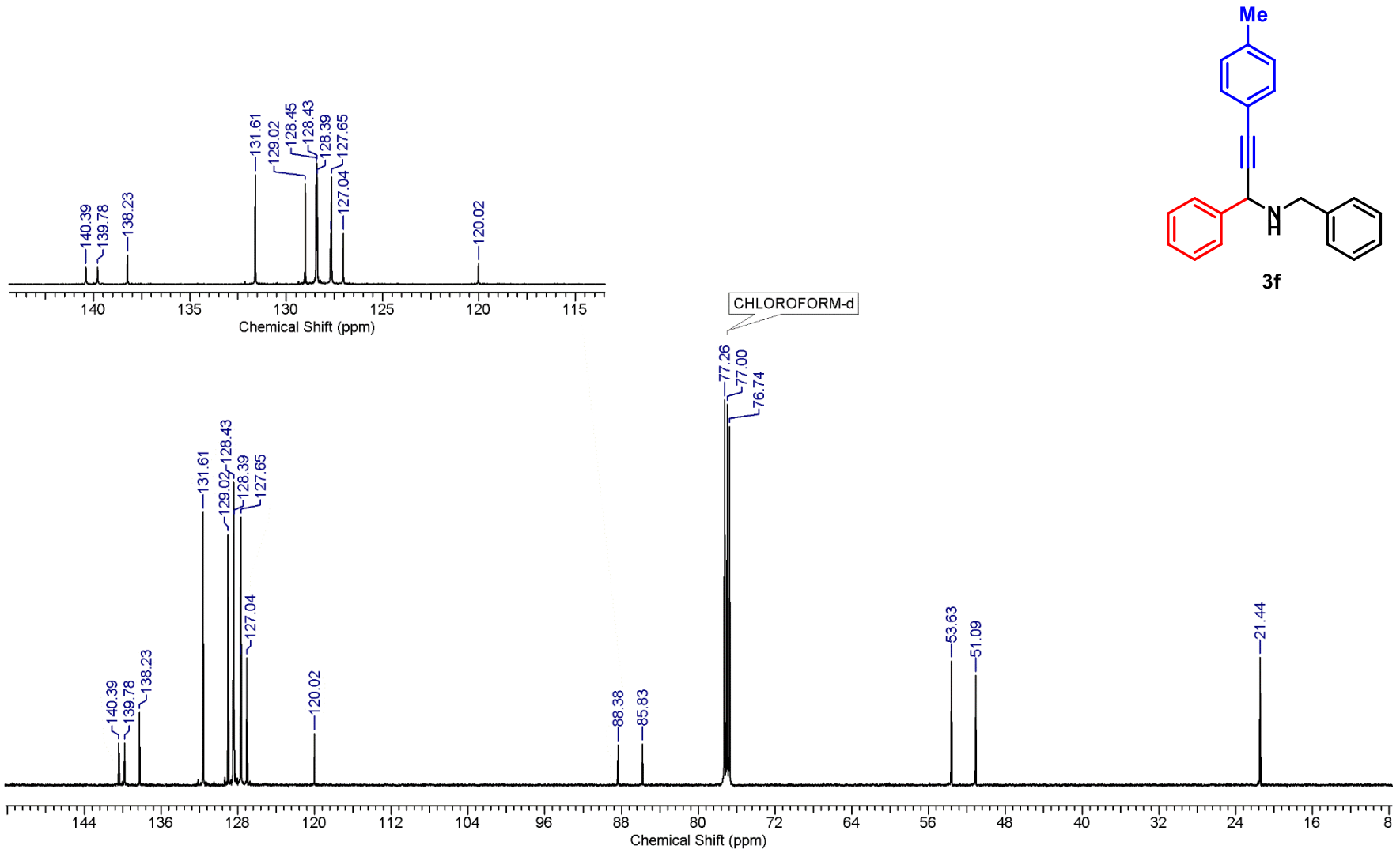

CHLOROFORM-d
139.82
137.38
131.69
129.14
128.38
128.23
127.50
127.00
123.18
89.41
85.46
77.26
77.00
76.74
53.59
53.34
51.05
21.09
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

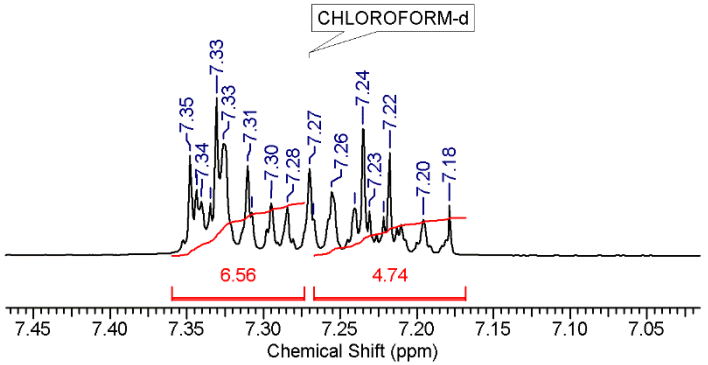

Me
N
H

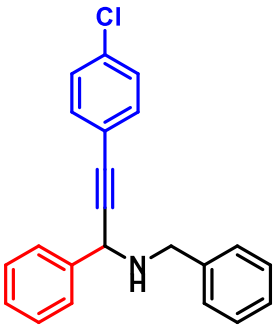
3f


CHLOROFORM-d
7.56
7.56
7.56
7.54
7.54
7.36
7.35
7.34
7.33
7.31
7.31
7.29
7.27
7.27
7.25
7.23
7.19
7.19
7.08
7.06
2.00
5.53
1.13
0.91
1.02
1.04
2.01
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)

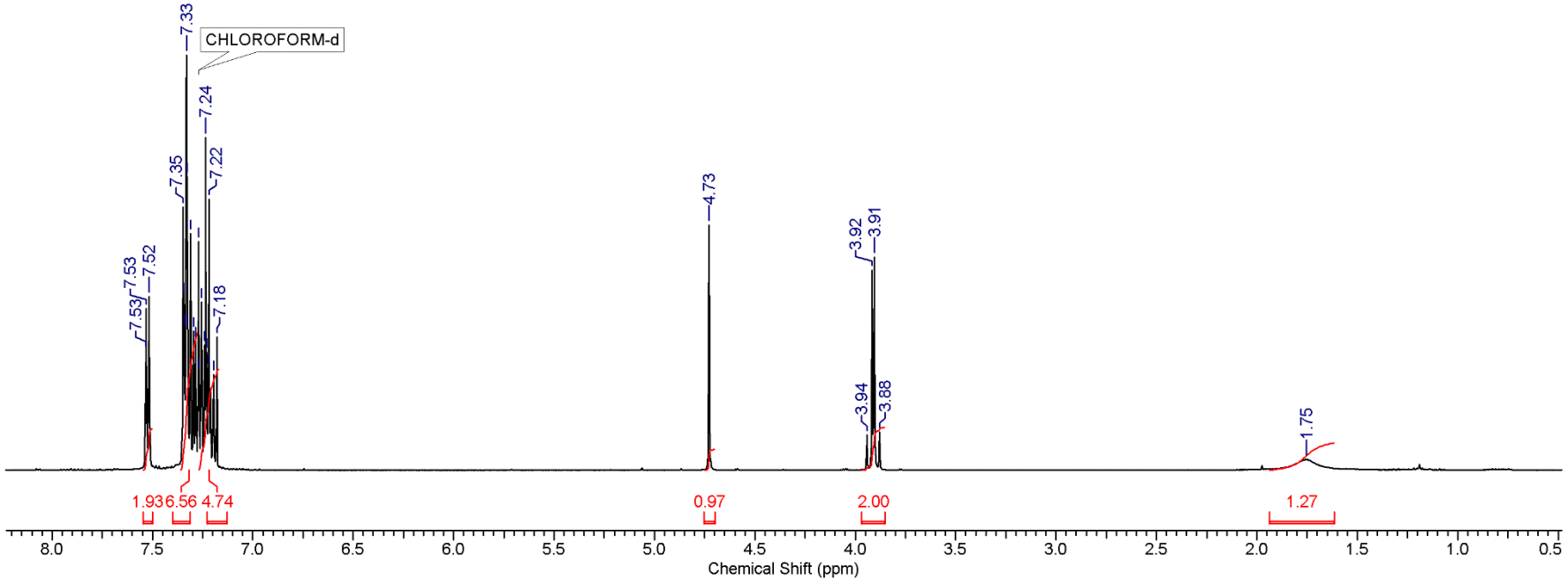

CHLOROFORM-d
7.56
7.56
7.54
7.34
7.33
7.31
7.31
7.27
7.19
7.08
7.06
7.36
4.74
3.93
3.93
2.29
1.70
2.00
5.53
1.13
0.91
1.02
1.04
2.01
1.02
2.07
3.01
1.45
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

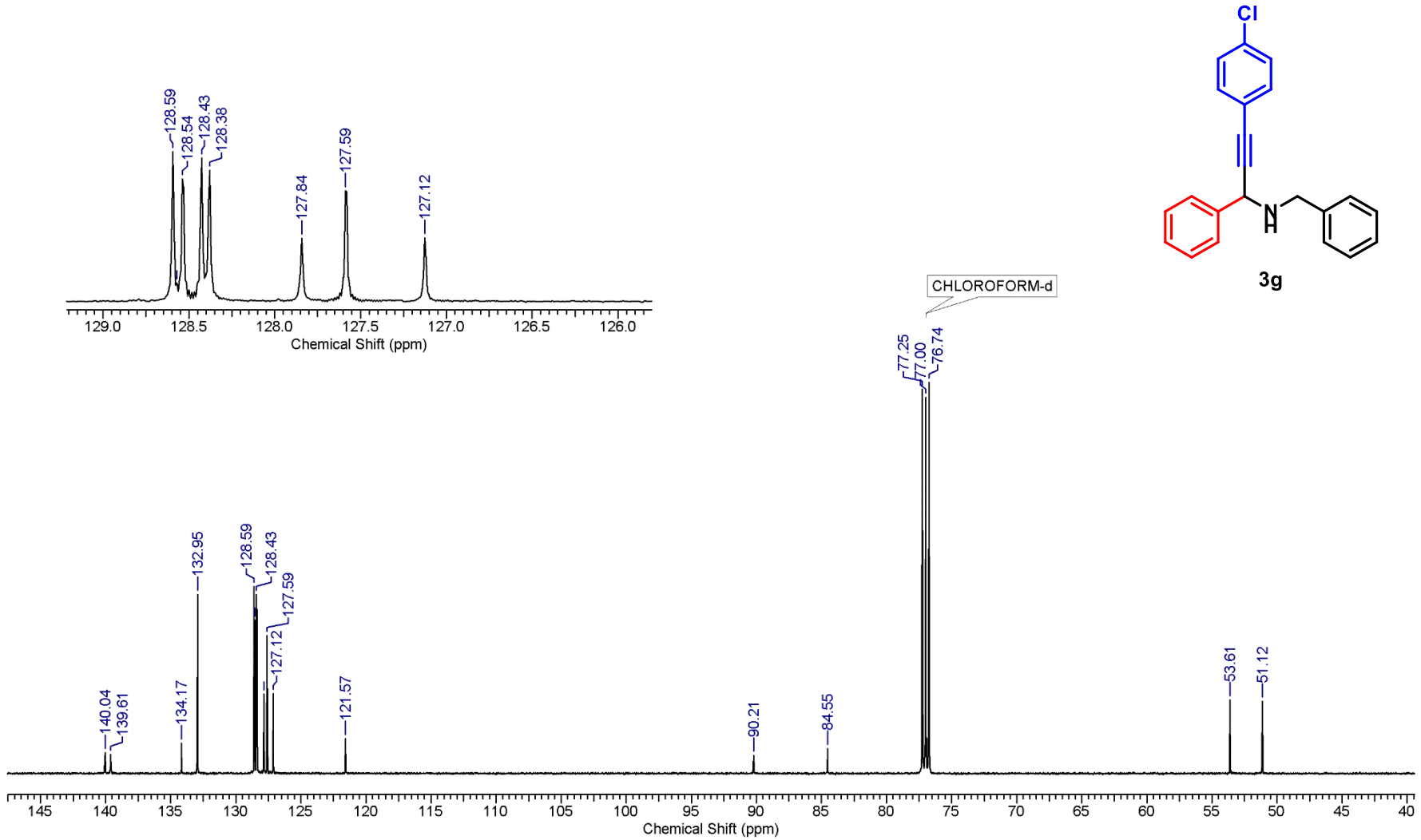

Me
N
H
3f
CHLOROFORM-d
140.39
139.78
138.23
131.61
129.02
128.45
128.43
128.39
127.65
127.04
120.02
88.38
85.83
77.26
77.00
76.74
53.63
51.09
21.44
Chemical Shift (ppm)

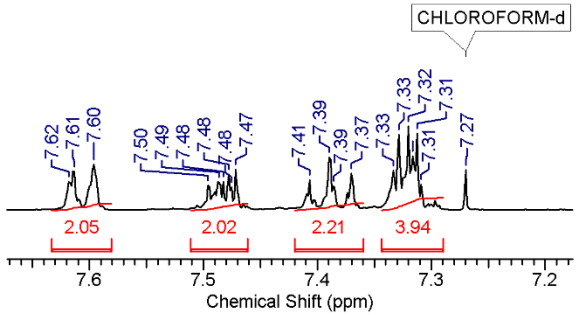

CHLOROFORM-d
7.35
7.34
7.33
7.33
7.31
7.30
7.28
7.27
7.26
7.24
7.23
7.22
7.20
7.18
6.56
4.74
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
Chemical Shift (ppm)

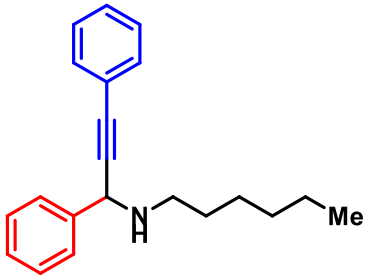

Cl
N
H

**3g**

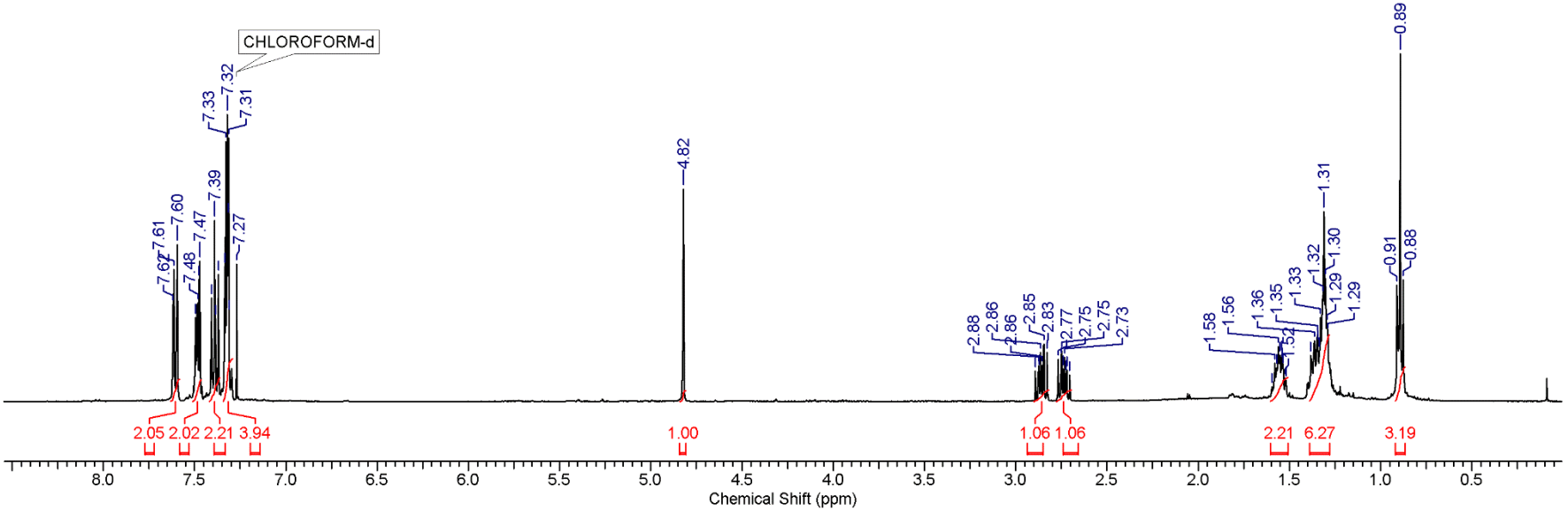

CHLOROFORM-d
7.53
7.52
7.53
7.35
7.33
7.24
7.22
7.18
4.73
3.92
3.91
3.94
3.88
1.75
1.93
6.56
4.74
0.97
2.00
1.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

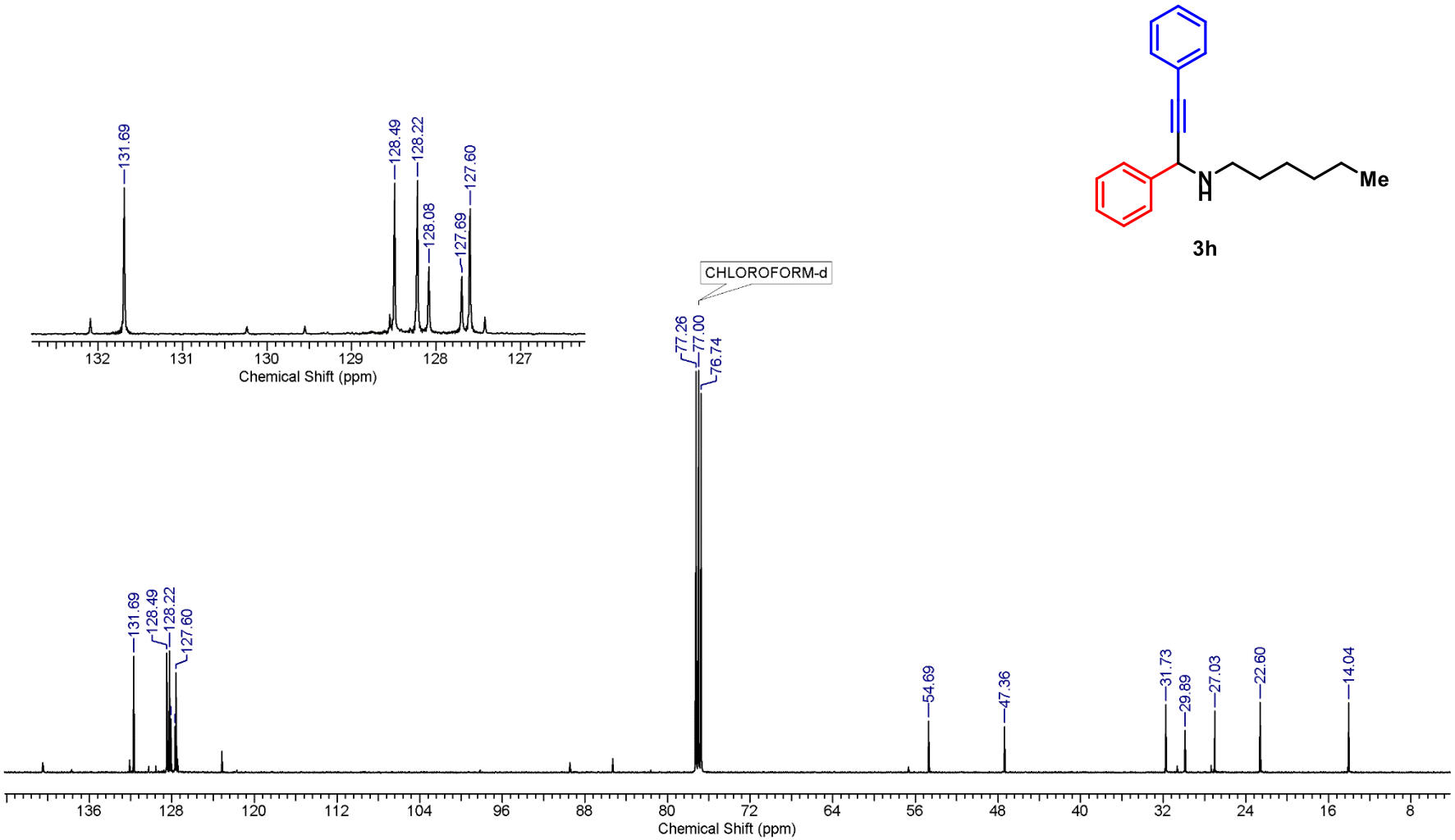

Cl
N
H
3g
CHLOROFORM-d
128.59
128.54
128.43
128.38
127.84
127.59
127.12
77.25
77.00
76.74
140.04
139.61
134.17
132.95
128.59
128.43
127.59
127.12
121.57
90.21
84.55
53.61
51.12
Chemical Shift (ppm)
Chemical Shift (ppm)

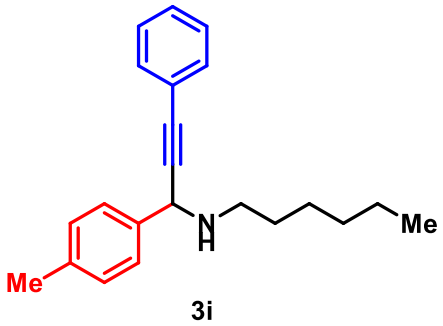

CHLOROFORM-d
7.62
7.61
7.60
7.50
7.49
7.48
7.48
7.48
7.47
7.41
7.39
7.39
7.37
7.33
7.33
7.32
7.31
7.31
7.27
2.05
2.02
2.21
3.94
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)


N
H
Me

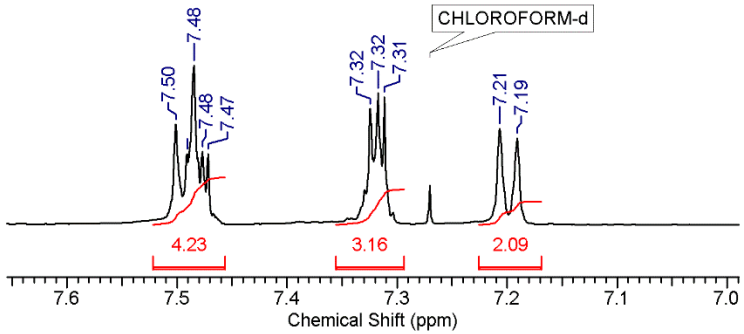
3h

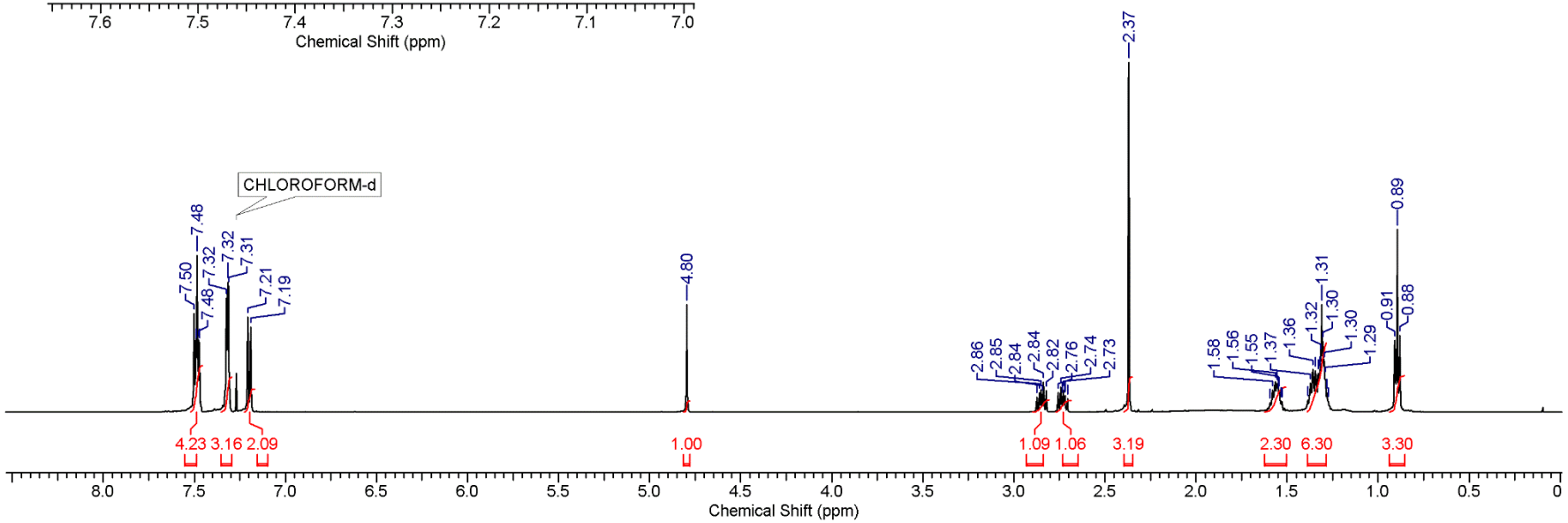

CHLOROFORM-d
7.62
7.61
7.60
7.48
7.47
7.39
7.33
7.32
7.31
7.27
4.82
2.88
2.86
2.86
2.85
2.83
2.77
2.75
2.75
2.73
1.58
1.56
1.36
1.35
1.33
1.54
1.32
1.31
1.30
1.29
1.29
0.91
0.89
0.88
2.05
2.02
2.21
3.94
1.00
1.06
1.06
2.21
6.27
3.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

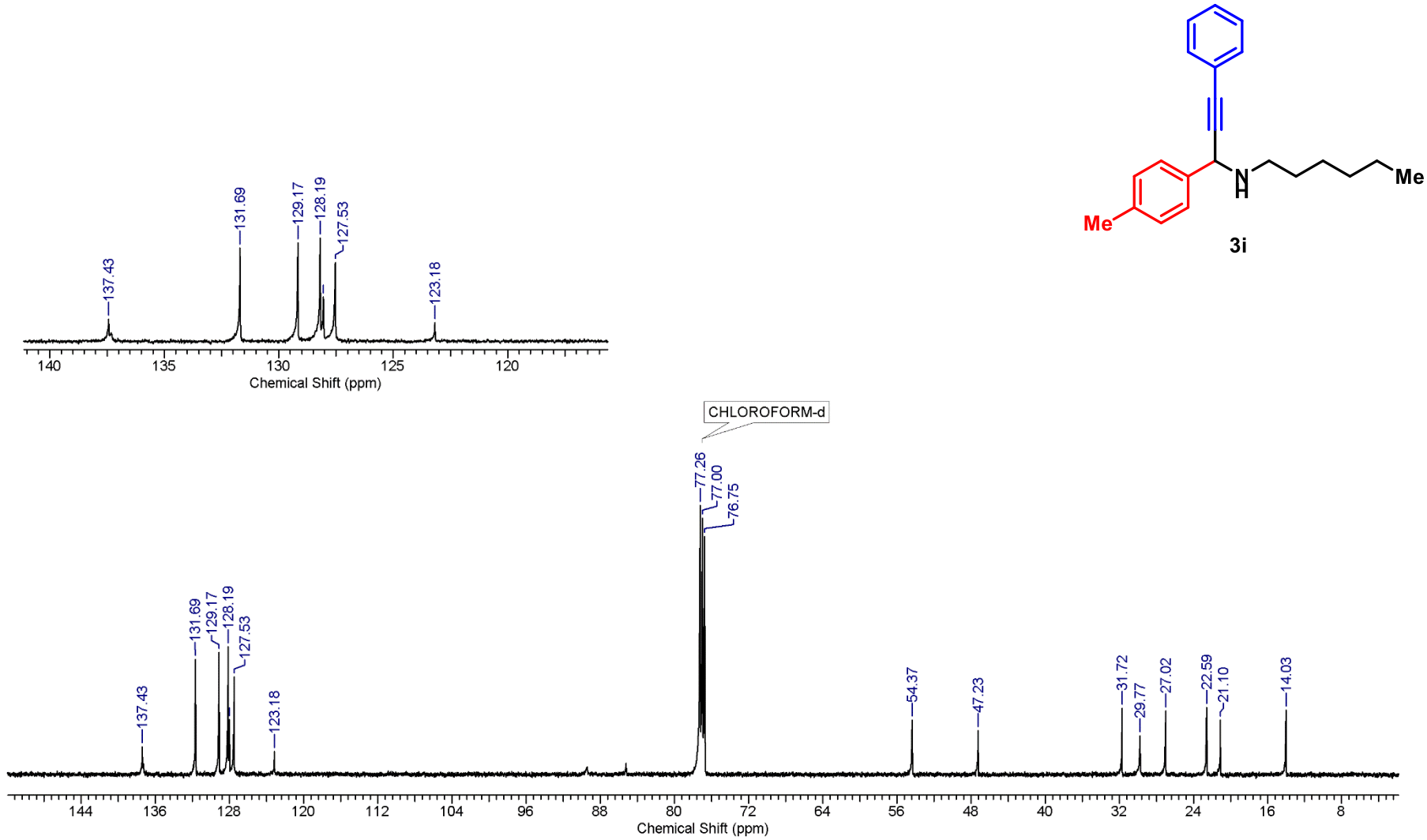

131.69
128.49
128.22
128.08
127.69
127.60
132
131
130
129
128
127
Chemical Shift (ppm)
CHLOROFORM-d
77.26
77.00
76.74
54.69
47.36
31.73
29.89
27.03
22.60
14.04
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)
N
H
Me
3h


Me
N
H
Me

3i

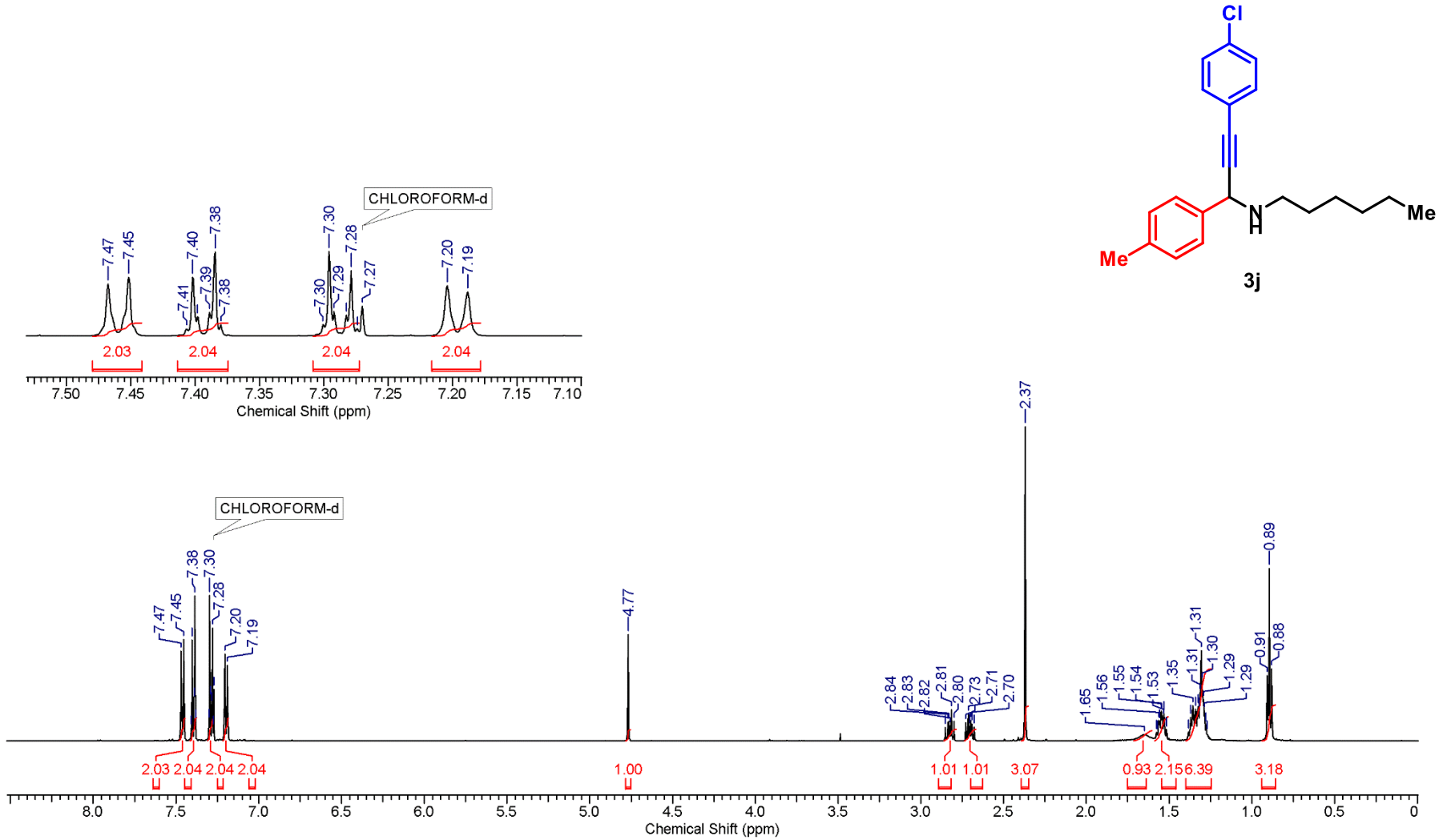

CHLOROFORM-d
7.50
7.48
7.48
7.47
7.32
7.32
7.31
7.21
7.19
4.23
3.16
2.09
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)

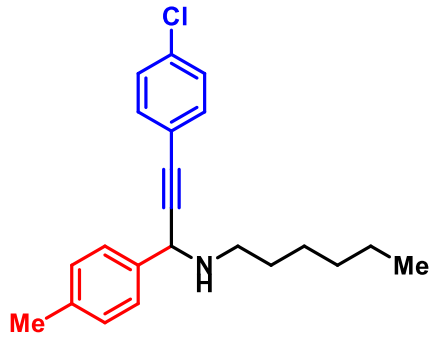

CHLOROFORM-d
7.50
7.48
7.48
7.32
7.32
7.31
7.21
7.19
4.80
2.86
2.85
2.84
2.84
2.82
2.76
2.74
2.73
2.37
1.58
1.56
1.55
1.37
1.36
1.32
1.31
1.30
1.30
1.29
0.91
0.89
0.88
4.23
3.16
2.09
1.00
1.09
1.06
3.19
2.30
6.30
3.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


137.43
131.69
129.17
128.19
127.53
123.18
140
135
130
125
120
Chemical Shift (ppm)
CHLOROFORM-d
77.26
77.00
76.75
137.43
131.69
129.17
128.19
127.53
123.18
54.37
47.23
31.72
29.77
27.02
22.59
21.10
14.03
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

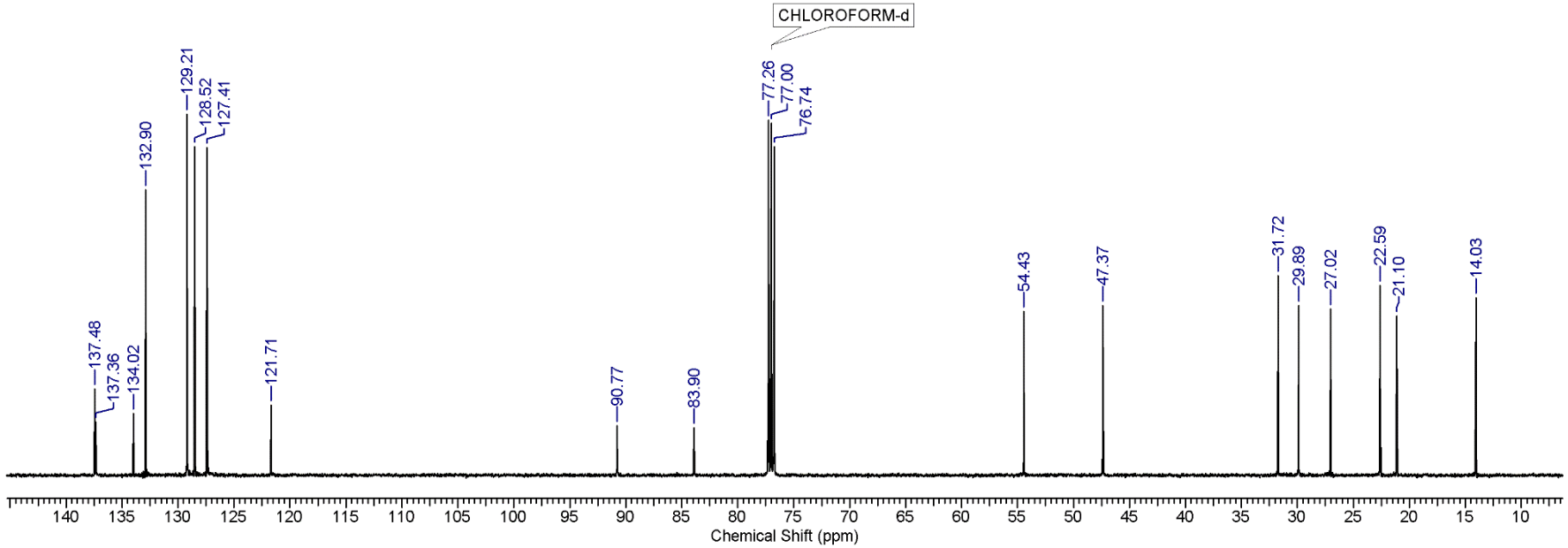

Me
N
H
Me

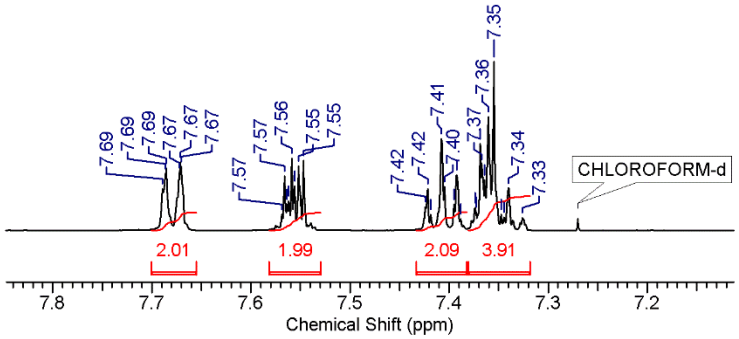
3i

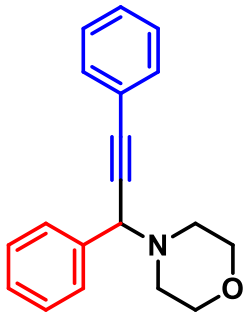

Cl
Me
N
H
Me
3j
CHLOROFORM-d
7.47
7.45
7.41
7.40
7.39
7.38
7.38
7.30
7.30
7.29
7.28
7.27
7.20
7.19
2.03
2.04
2.04
2.04
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
Chemical Shift (ppm)
CHLOROFORM-d
7.47
7.45
7.38
7.38
7.30
7.28
7.20
7.19
4.77
2.84
2.83
2.82
2.81
2.80
2.73
2.71
2.70
2.37
1.65
1.56
1.55
1.54
1.53
1.35
1.31
1.31
1.30
1.29
1.29
0.91
0.89
0.88
2.03
2.04
2.04
2.04
1.00
1.01
1.01
3.07
0.93
2.15
6.39
3.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Cl
N
H
Me
Me

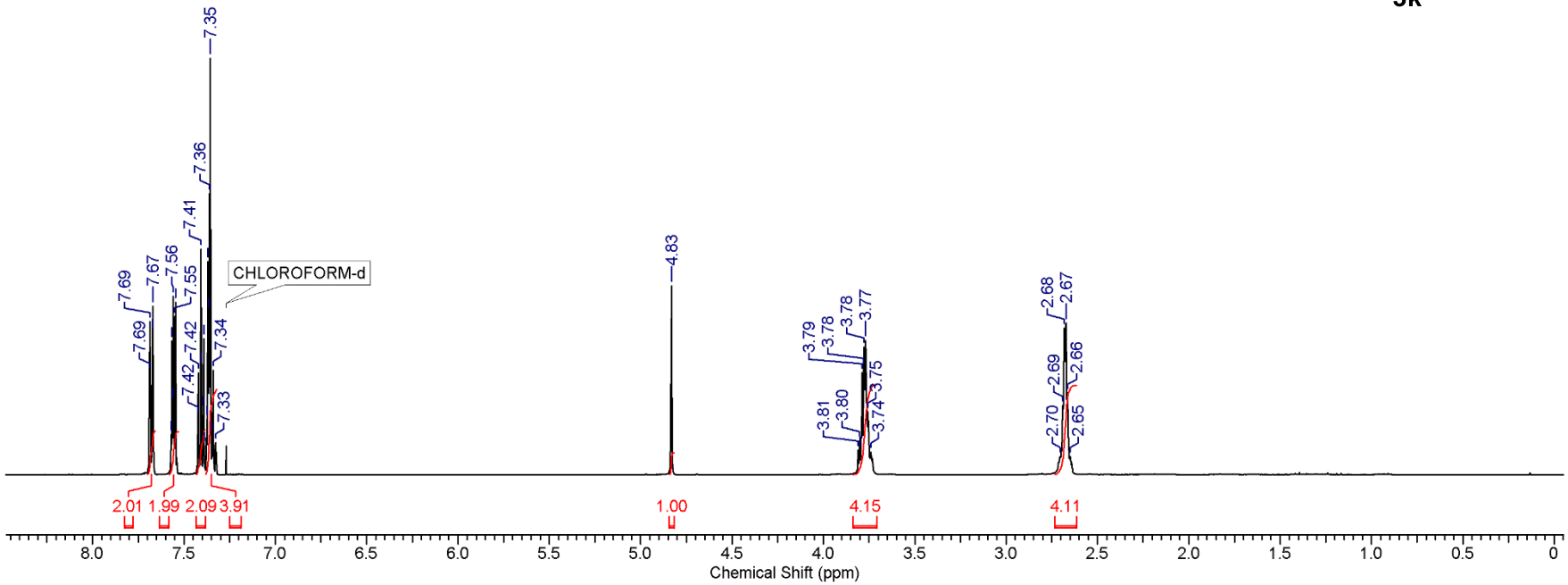
3j

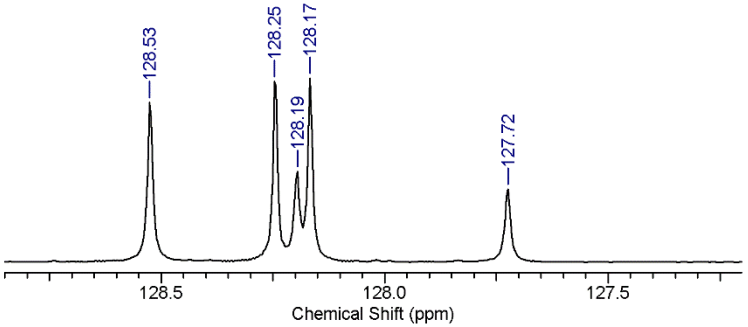

CHLOROFORM-d
137.48
137.36
134.02
132.90
129.21
128.52
127.41
121.71
90.77
83.90
77.26
77.00
76.74
54.43
47.37
31.72
29.89
27.02
22.59
21.10
14.03
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
Chemical Shift (ppm)

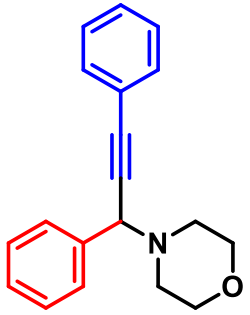

7.69
7.69
7.69
7.67
7.67
7.67
7.57
7.57
7.56
7.55
7.55
7.42
7.42
7.41
7.40
7.37
7.36
7.35
7.34
7.33
CHLOROFORM-d
2.01
1.99
2.09
3.91
7.8
7.7
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)


N
O

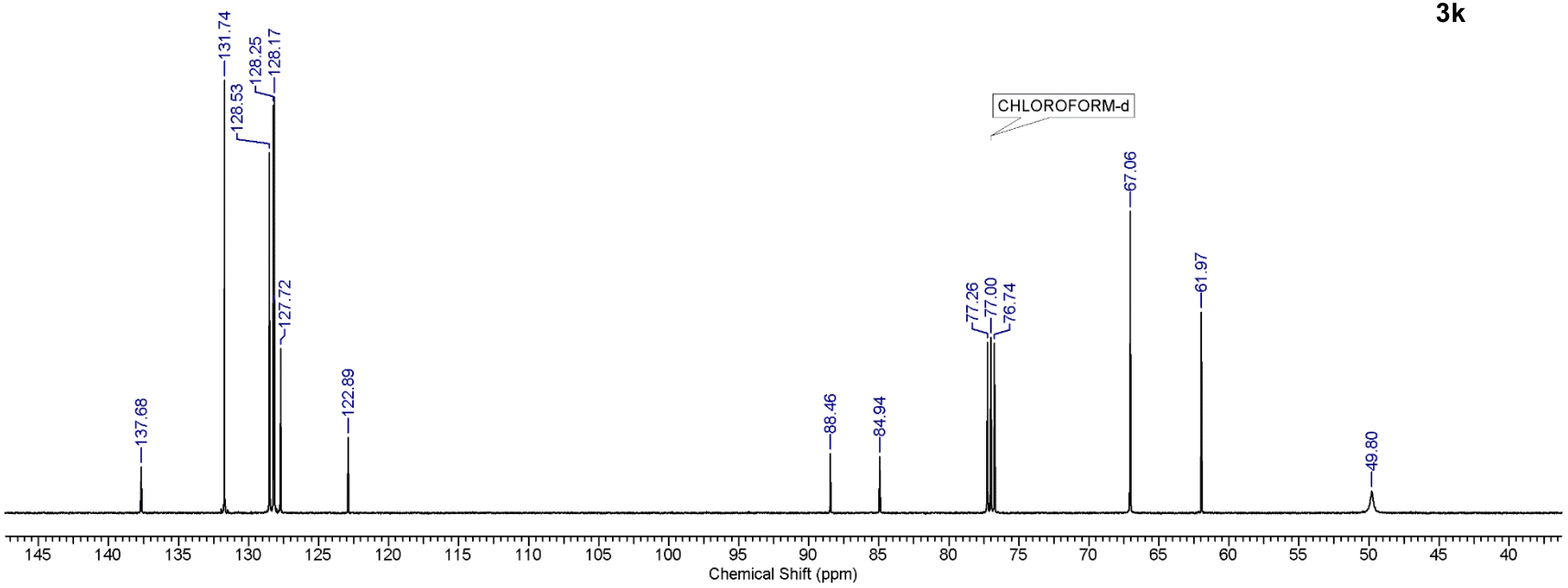
**3k**

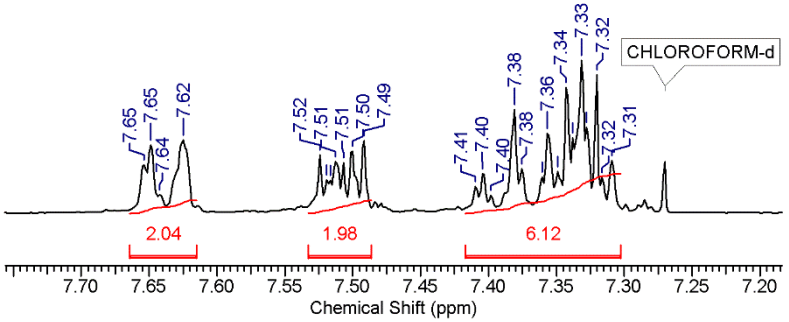

7.35
7.36
7.41
7.69
7.67
7.56
7.55
7.42
7.34
7.33
CHLOROFORM-d
4.83
3.79
3.78
3.78
3.77
3.81
3.80
3.75
3.74
2.68
2.67
2.69
2.66
2.70
2.65
2.01
1.99
2.09
3.91
1.00
4.15
4.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

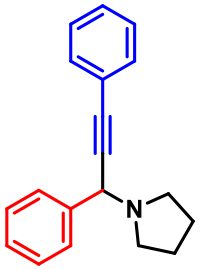

128.53
128.25
128.17
128.19
127.72
128.5
128.0
127.5
Chemical Shift (ppm)


N
O

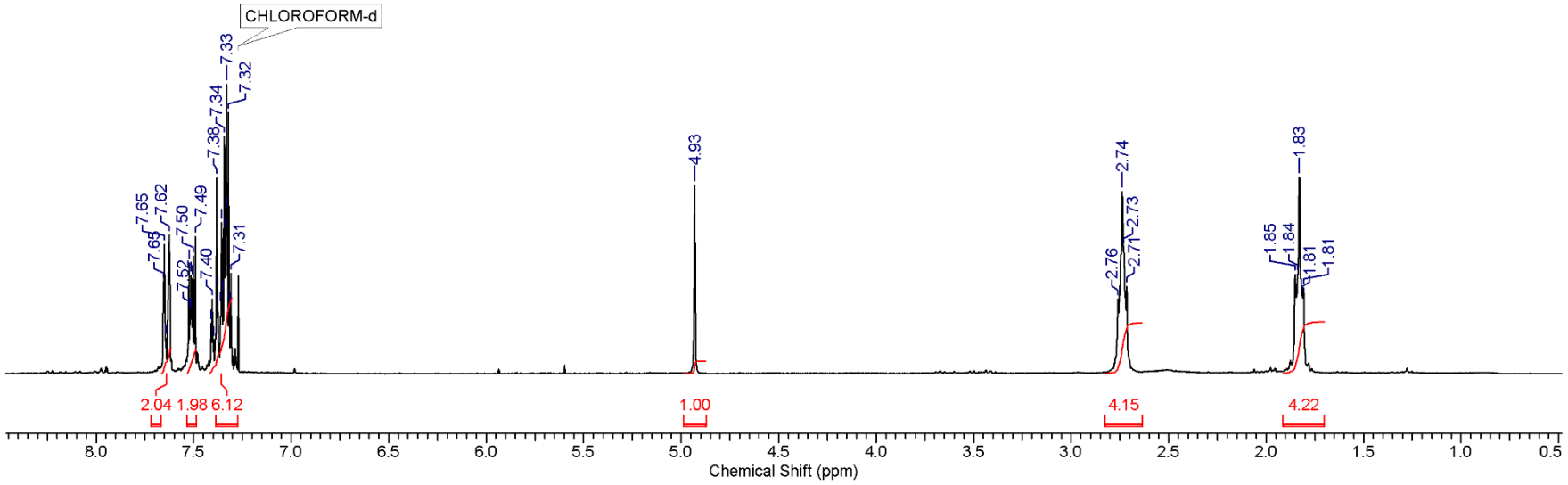
**3k**

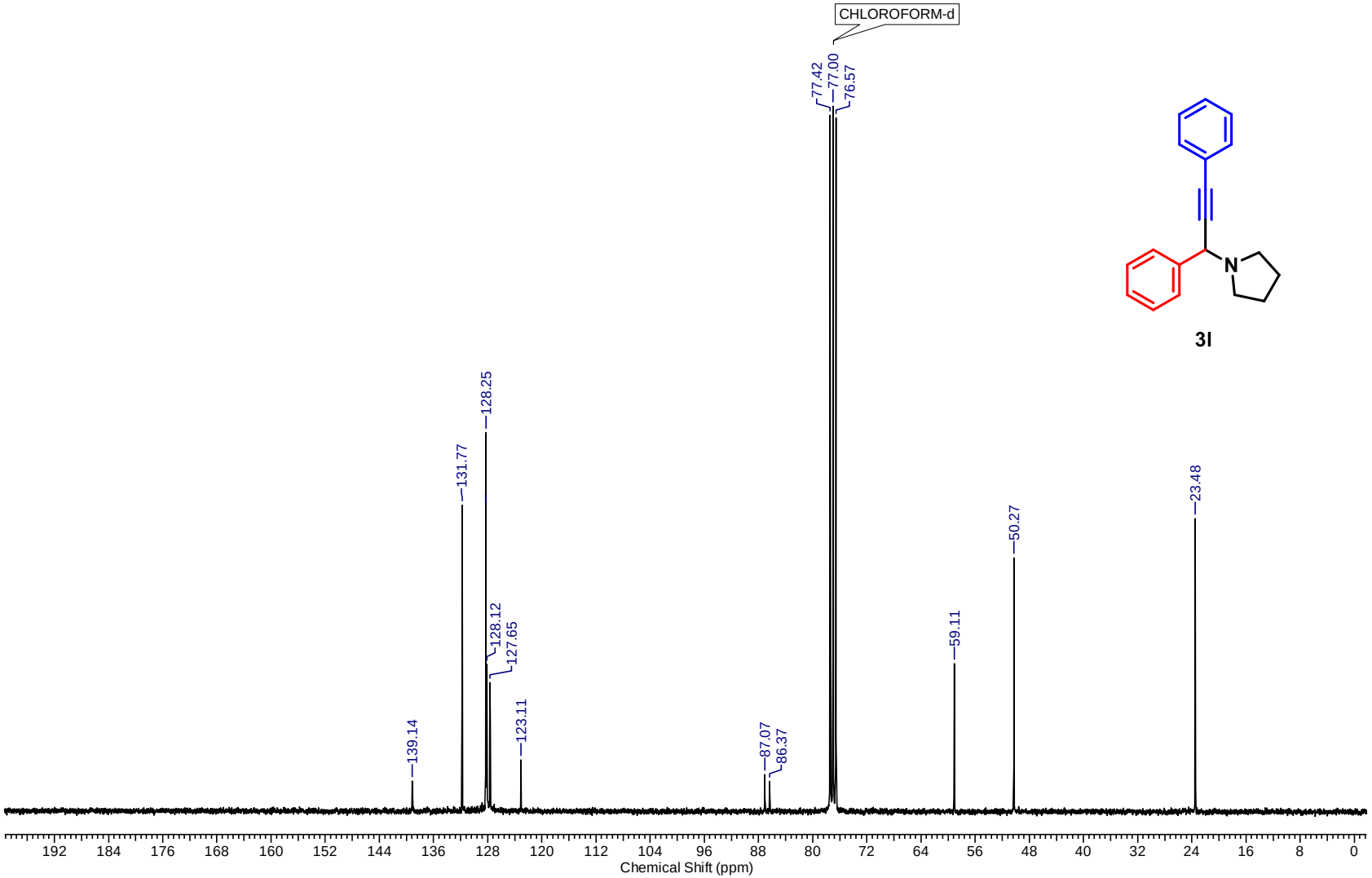

131.74
128.25
128.17
128.53
127.72
122.89
137.68
88.46
84.94
77.26
77.00
76.74
CHLOROFORM-d
67.06
61.97
49.80
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
Chemical Shift (ppm)

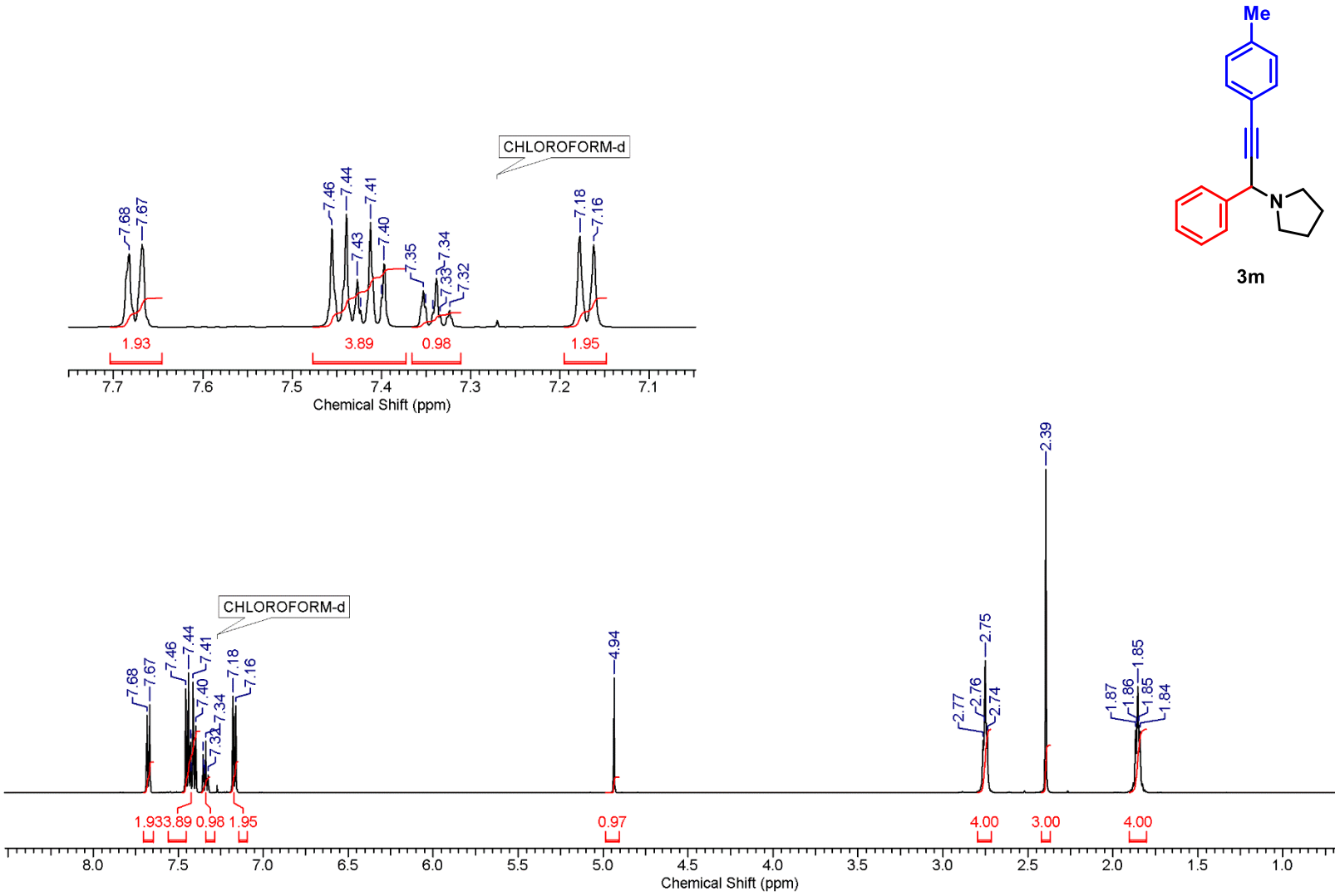

CHLOROFORM-d
7.65
7.65
7.64
7.62
7.52
7.51
7.51
7.50
7.49
7.41
7.40
7.40
7.38
7.38
7.36
7.34
7.33
7.32
7.32
7.31
2.04
1.98
6.12
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
Chemical Shift (ppm)

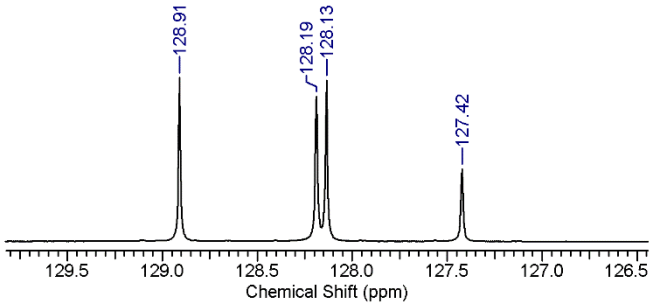

N

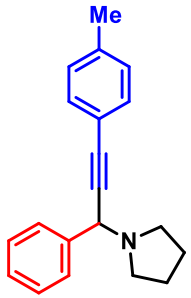
**3l**


CHLOROFORM-d
7.65
7.62
7.50
7.49
7.40
7.31
7.38
7.34
7.33
7.32
4.93
2.76
2.74
2.73
2.71
1.85
1.84
1.83
1.81
1.81
2.04
1.98
6.12
1.00
4.15
4.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

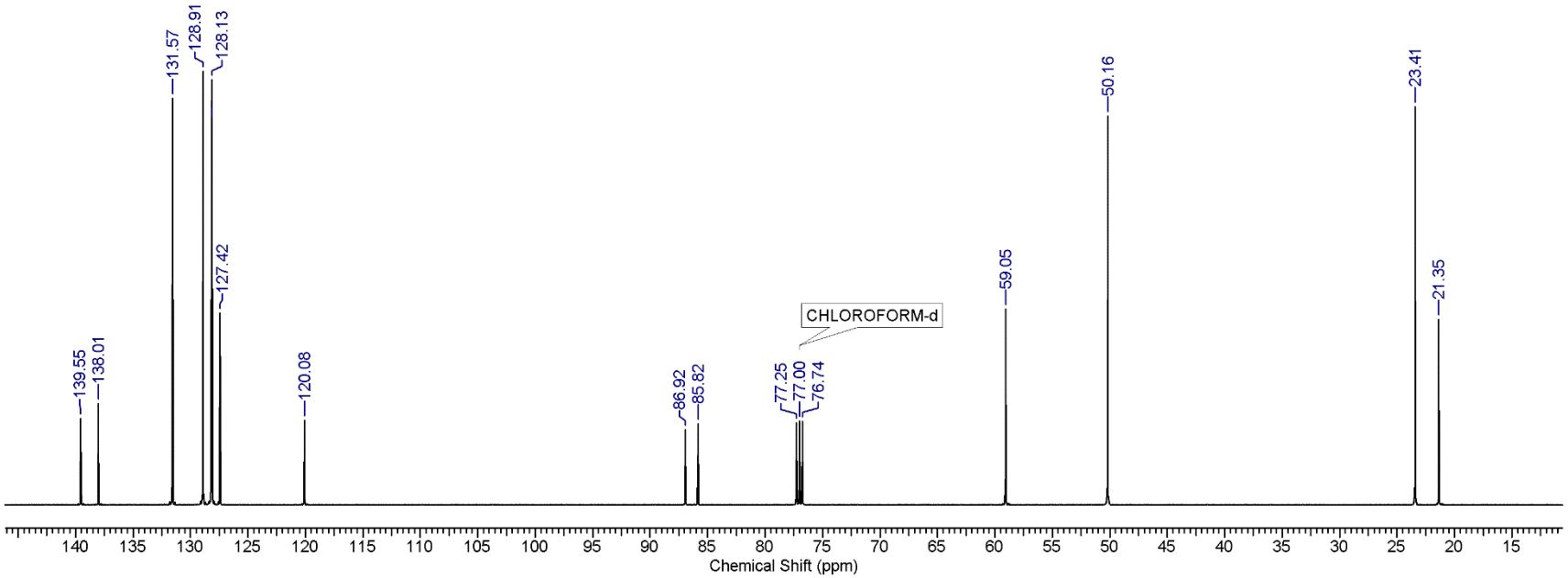

CHLOROFORM-d
77.42
77.00
76.57
128.25
131.77
128.12
127.65
123.11
139.14
87.07
86.37
59.11
50.27
23.48
N
3l
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

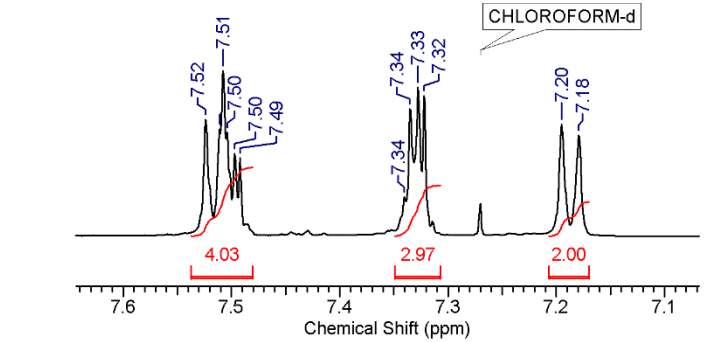

Me
N
3m
CHLOROFORM-d
7.68
7.67
7.46
7.44
7.41
7.40
7.35
7.34
7.33
7.32
7.18
7.16
1.93
3.89
0.98
1.95
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
CHLOROFORM-d
4.94
2.77
2.76
2.75
2.74
2.39
1.87
1.86
1.85
1.84
0.97
4.00
3.00
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

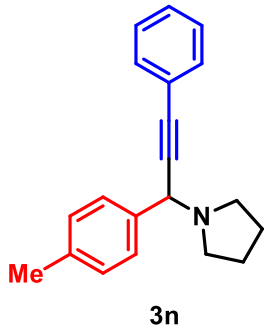

128.91
128.19
128.13
127.42
129.5
129.0
128.5
128.0
127.5
127.0
126.5
Chemical Shift (ppm)


Me
N

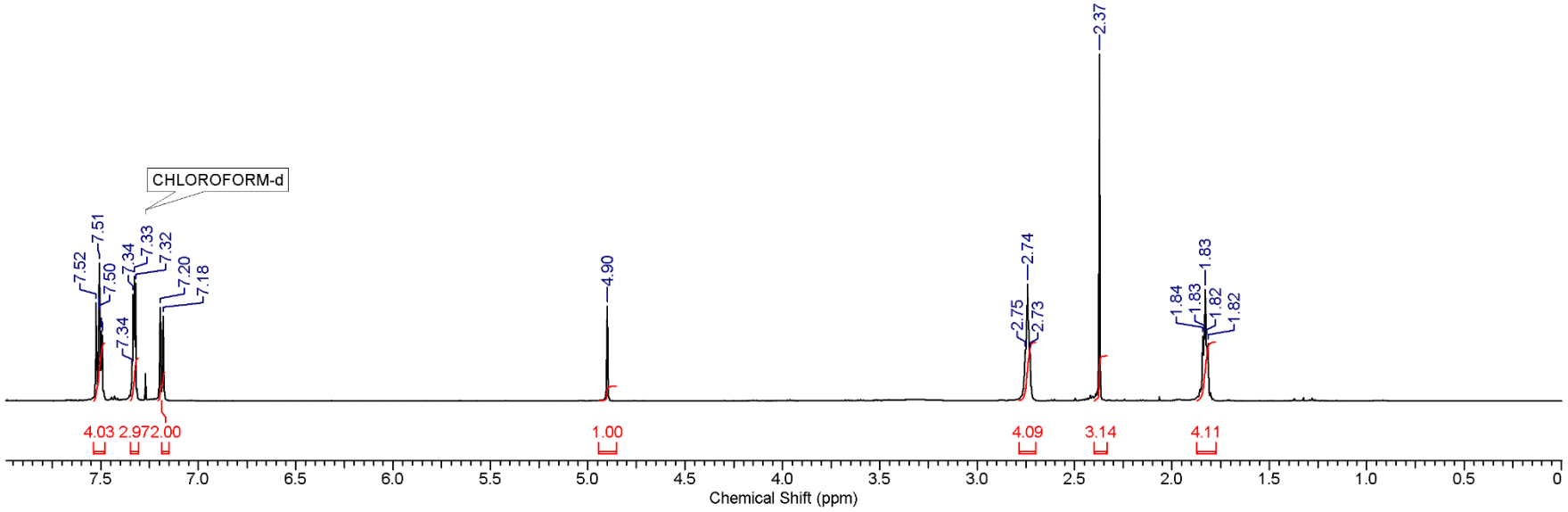
**3m**

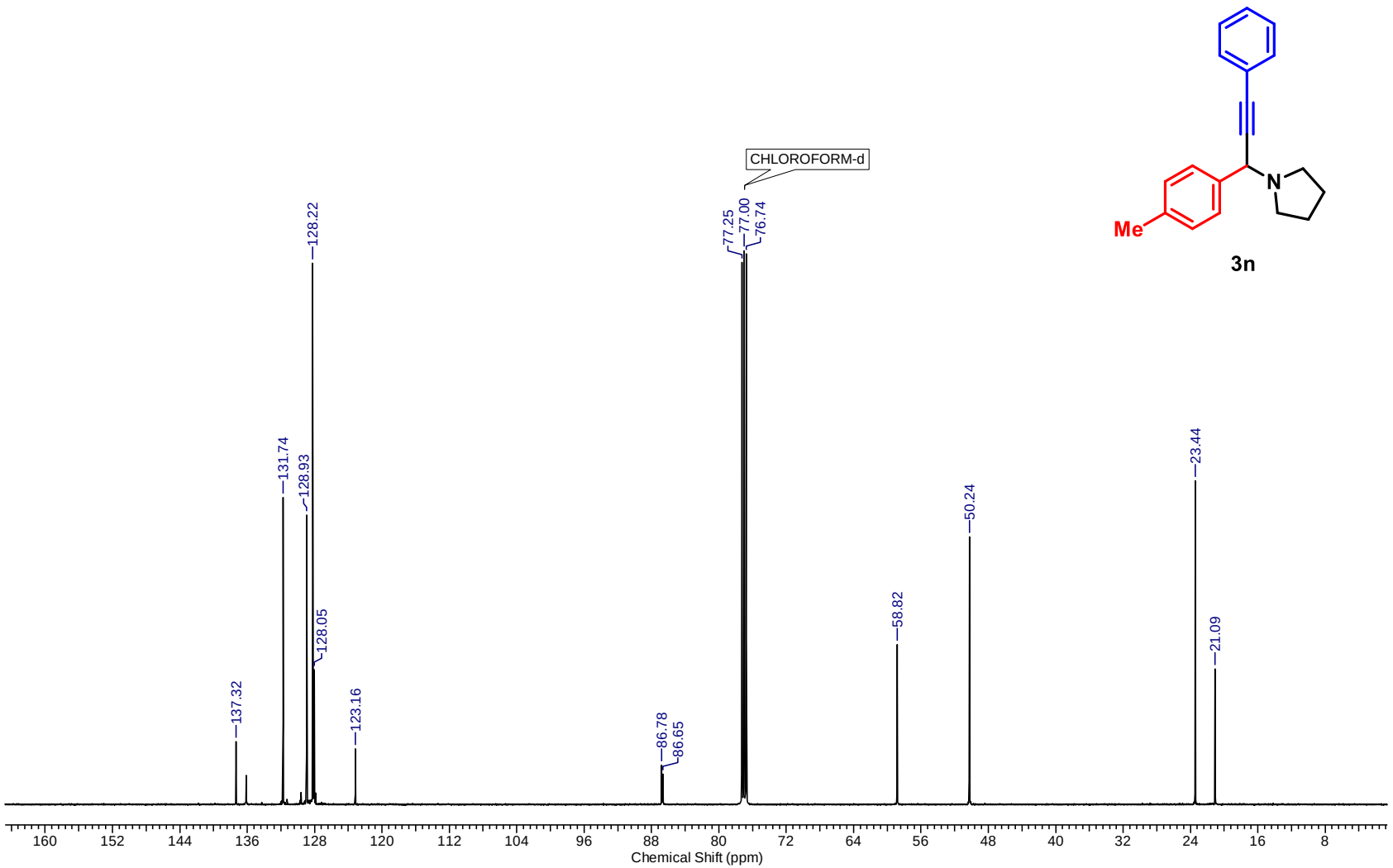

139.55
138.01
131.57
128.91
128.13
127.42
120.08
86.92
85.82
77.25
77.00
76.74
CHLOROFORM-d
59.05
50.16
23.41
21.35
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
Chemical Shift (ppm)

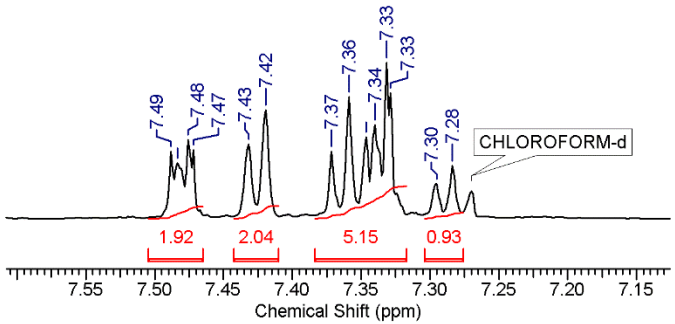

CHLOROFORM-d
7.52
7.51
7.50
7.50
7.49
7.34
7.33
7.32
7.34
7.20
7.18
4.03
2.97
2.00
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)

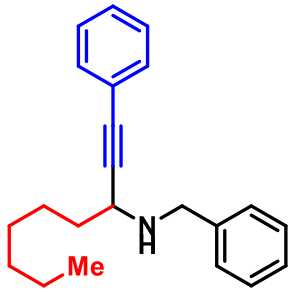

Me
N

**3n**

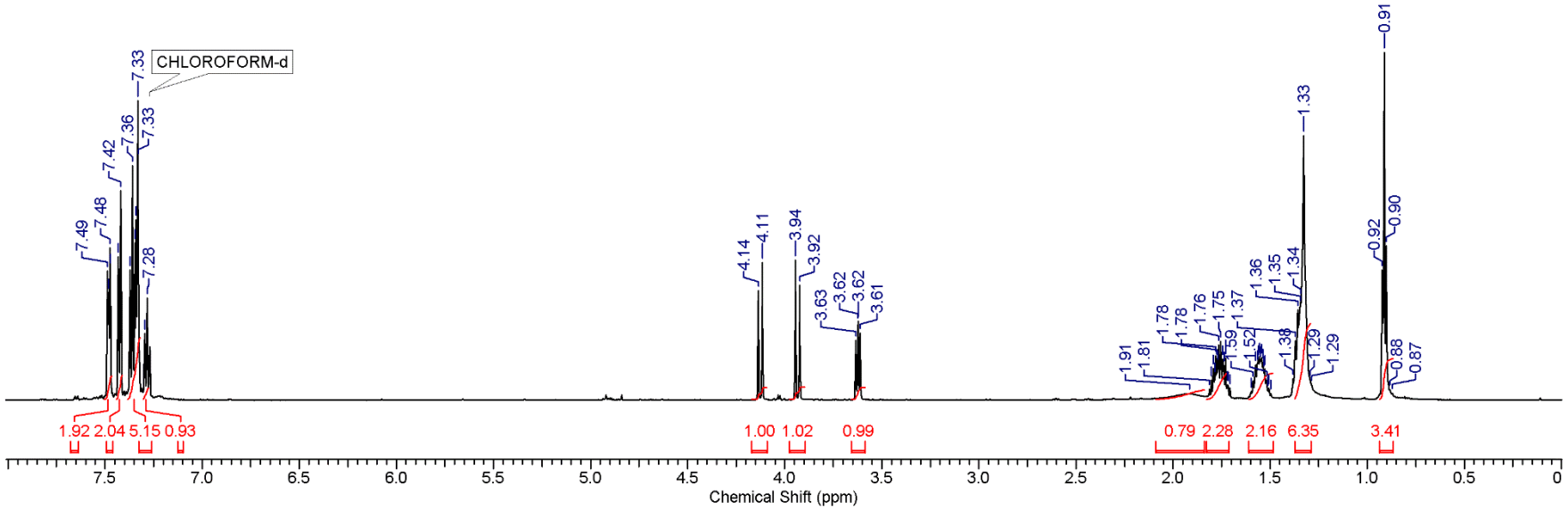

CHLOROFORM-d
7.52
7.51
7.50
7.34
7.34
7.33
7.32
7.20
7.18
4.90
2.75
2.74
2.73
2.37
1.84
1.83
1.82
1.82
1.83
4.03
2.97
2.00
1.00
4.09
3.14
4.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

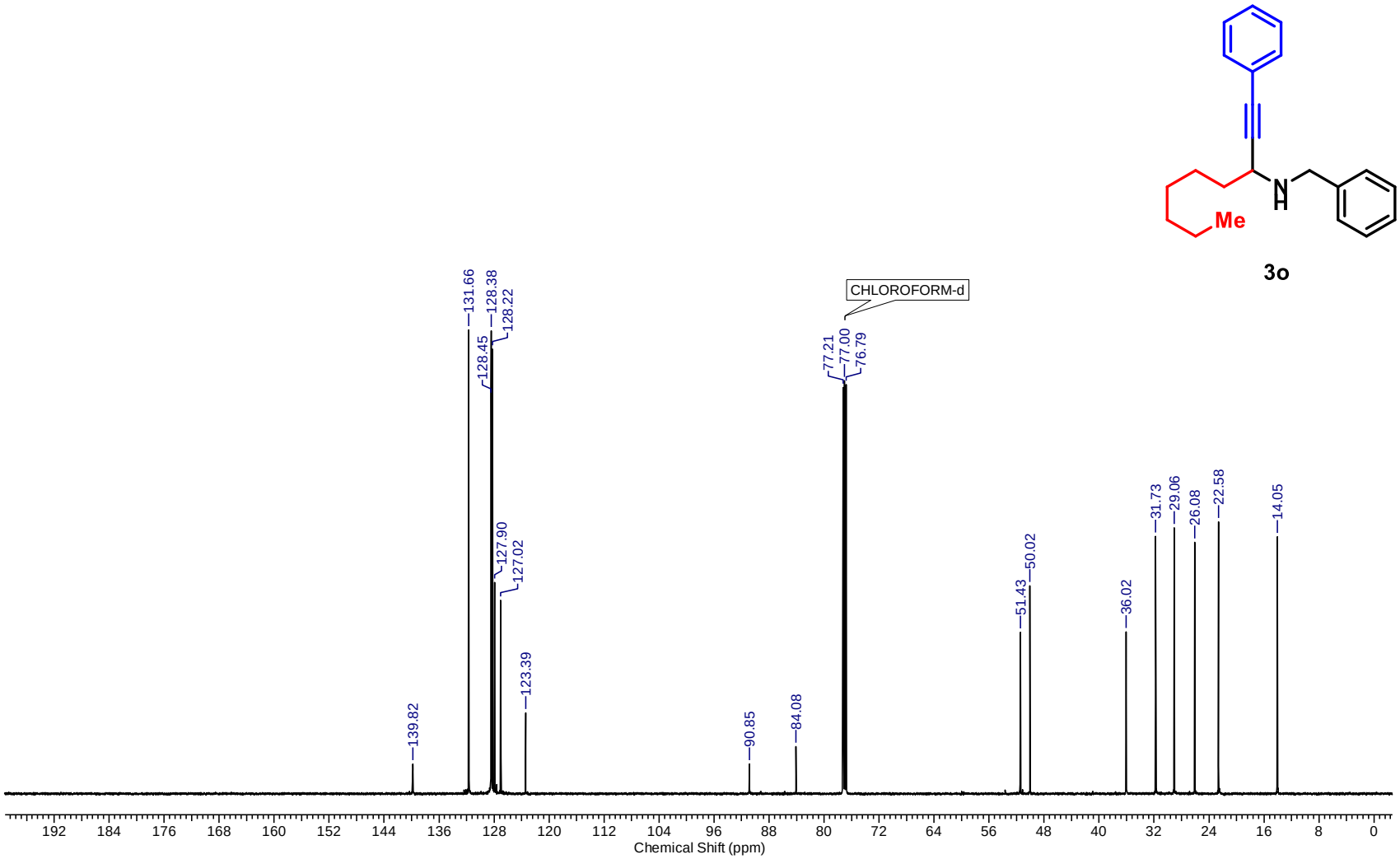

CHLOROFORM-d
77.25
77.00
76.74
128.22
131.74
128.93
128.05
137.32
123.16
86.78
86.65
58.82
50.24
23.44
21.09
Me
N
3n
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

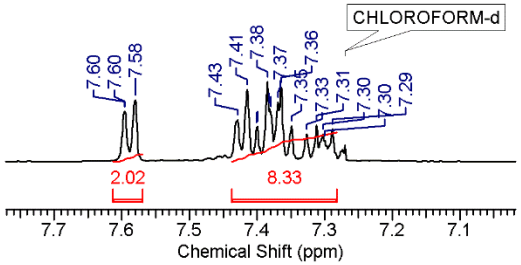

7.49
7.48
7.47
7.43
7.42
7.37
7.36
7.34
7.33
7.33
7.30
7.28
CHLOROFORM-d
1.92
2.04
5.15
0.93
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
Chemical Shift (ppm)

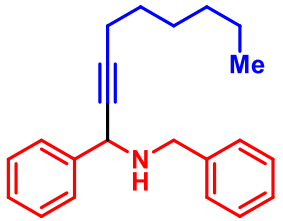

N
H
Me

**3o**

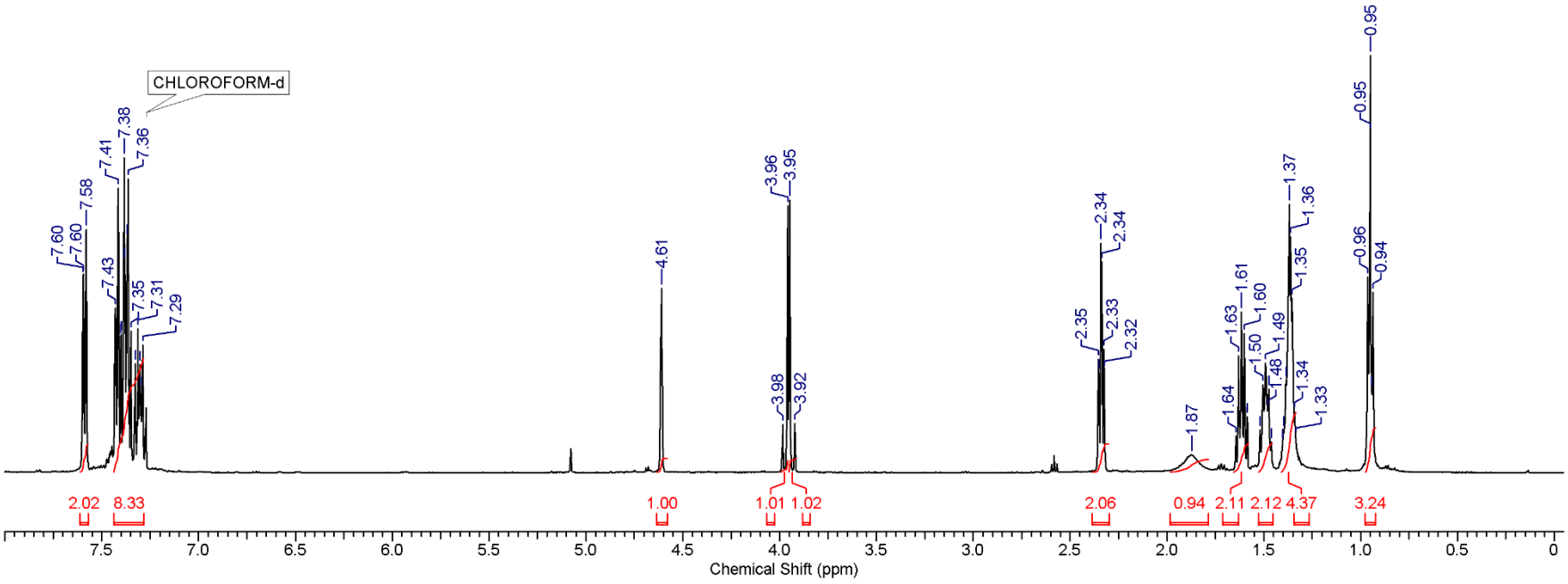

CHLOROFORM-d
7.49
7.48
7.42
7.36
7.33
7.33
7.28
4.14
4.11
3.94
3.92
3.63
3.62
3.62
3.61
1.91
1.81
1.78
1.78
1.76
1.75
1.59
1.52
1.37
1.36
1.35
1.34
1.38
1.33
1.29
1.29
0.92
0.91
0.90
0.88
0.87
1.92 2.04 5.15 0.93
1.00 1.02 0.99
0.79 2.28 2.16 6.35
3.41
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

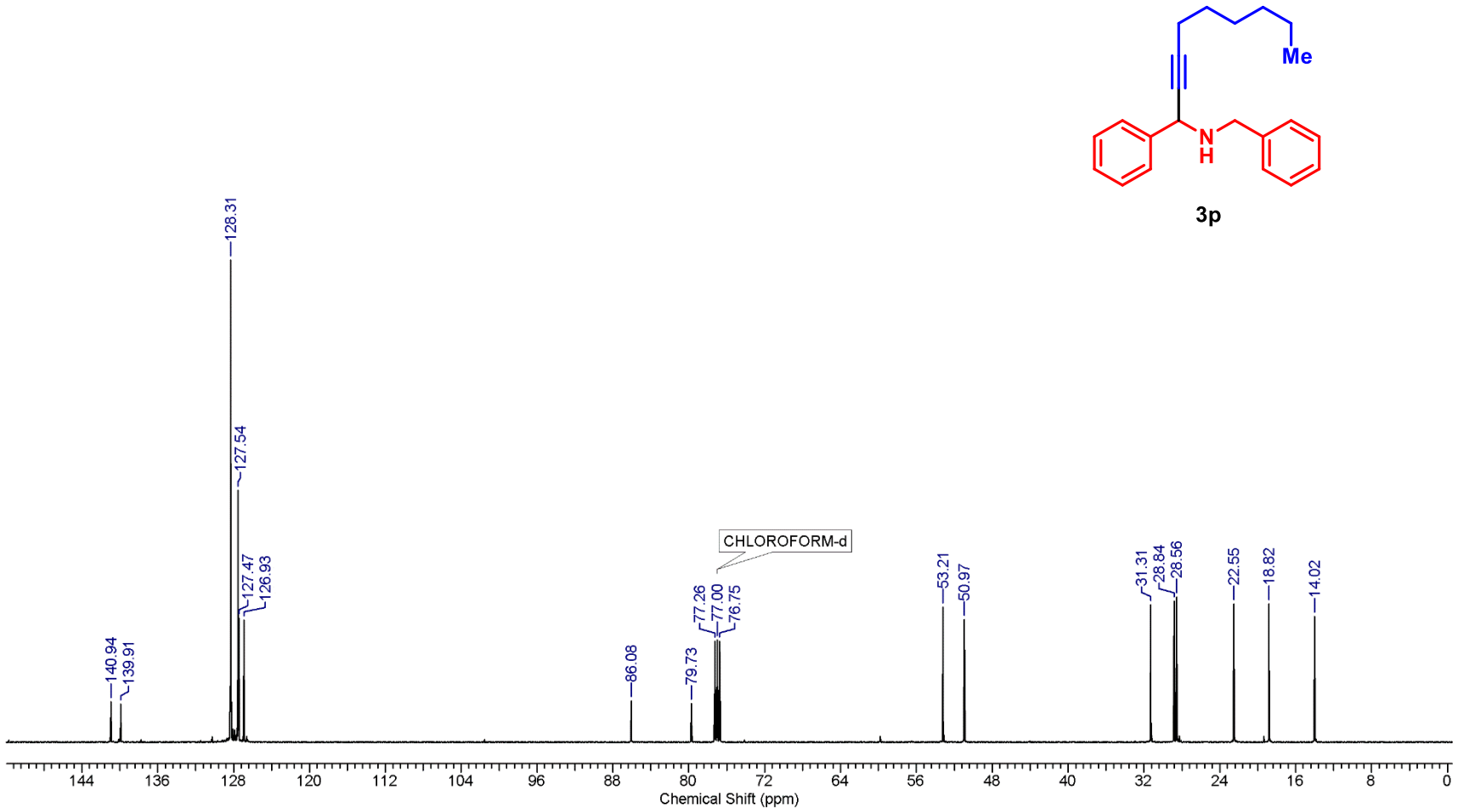

Me
N
H
3o
CHLOROFORM-d
131.66
128.38
128.22
128.45
127.90
127.02
123.39
139.82
90.85
84.08
77.21
77.00
76.79
51.43
50.02
36.02
31.73
29.06
26.08
22.58
14.05
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

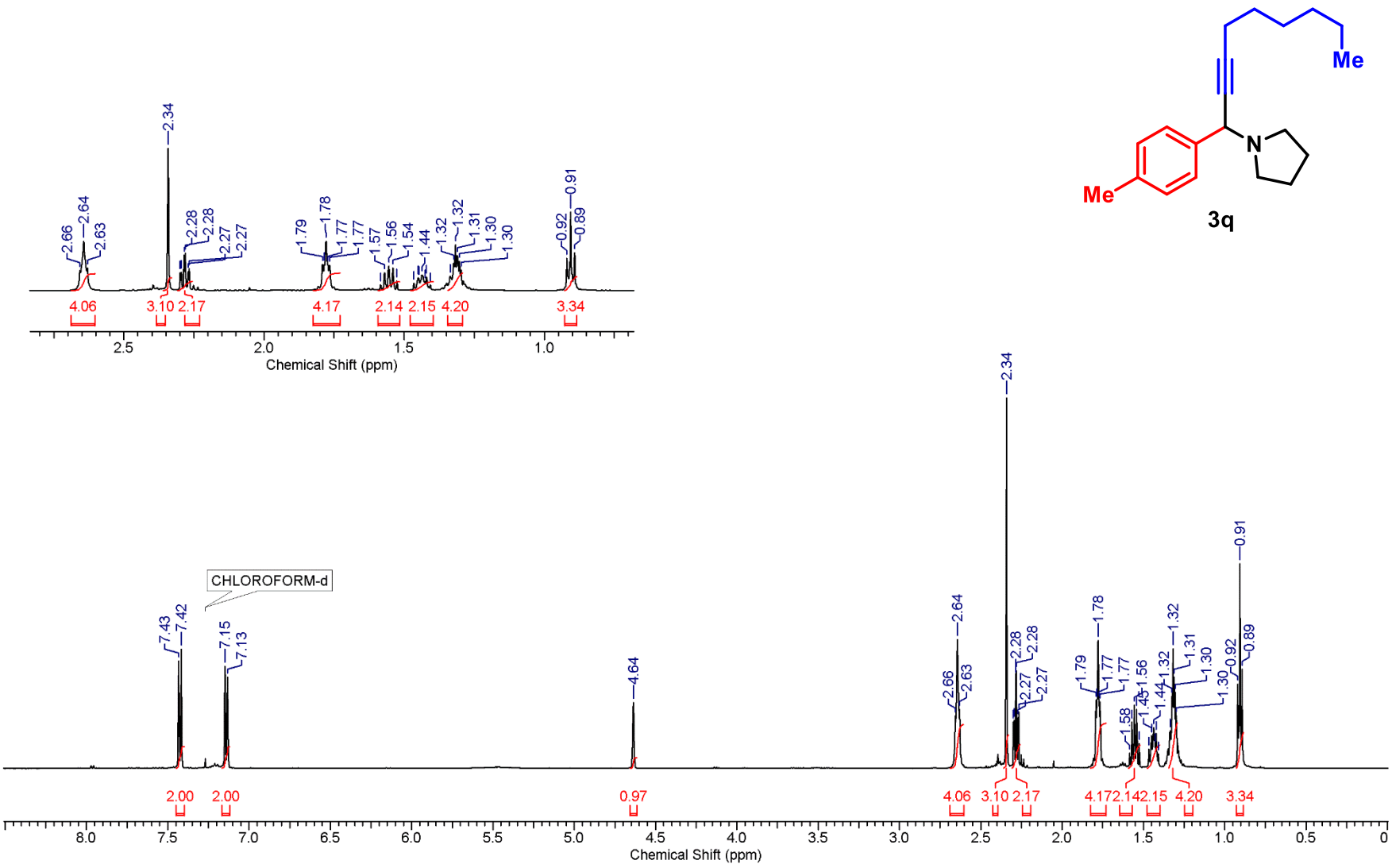

CHLOROFORM-d
7.60
7.60
7.58
7.43
7.41
7.38
7.37
7.36
7.35
7.33
7.31
7.30
7.30
7.29
2.02
8.33
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)

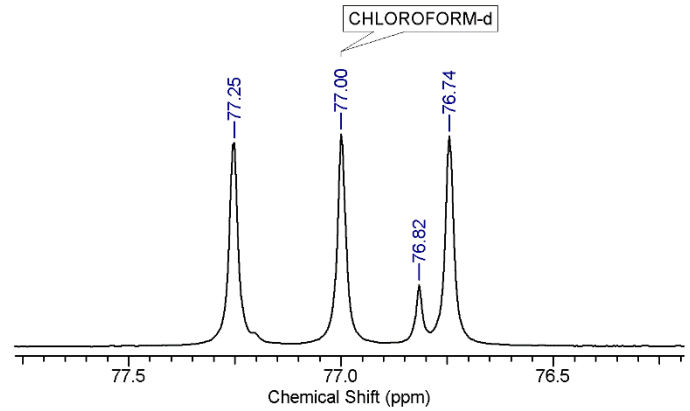

Me
N
H

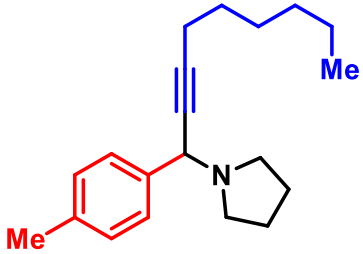
**3p**


CHLOROFORM-d
7.60
7.60
7.58
7.43
7.41
7.38
7.36
7.35
7.31
7.29
4.61
3.96
3.95
3.98
3.92
2.35
2.34
2.34
2.33
2.32
1.87
1.64
1.63
1.61
1.60
1.50
1.49
1.48
1.37
1.36
1.35
1.34
1.33
0.95
0.95
0.96
0.94
2.02
8.33
1.00
1.01
1.02
2.06
0.94
2.11
2.12
4.37
3.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

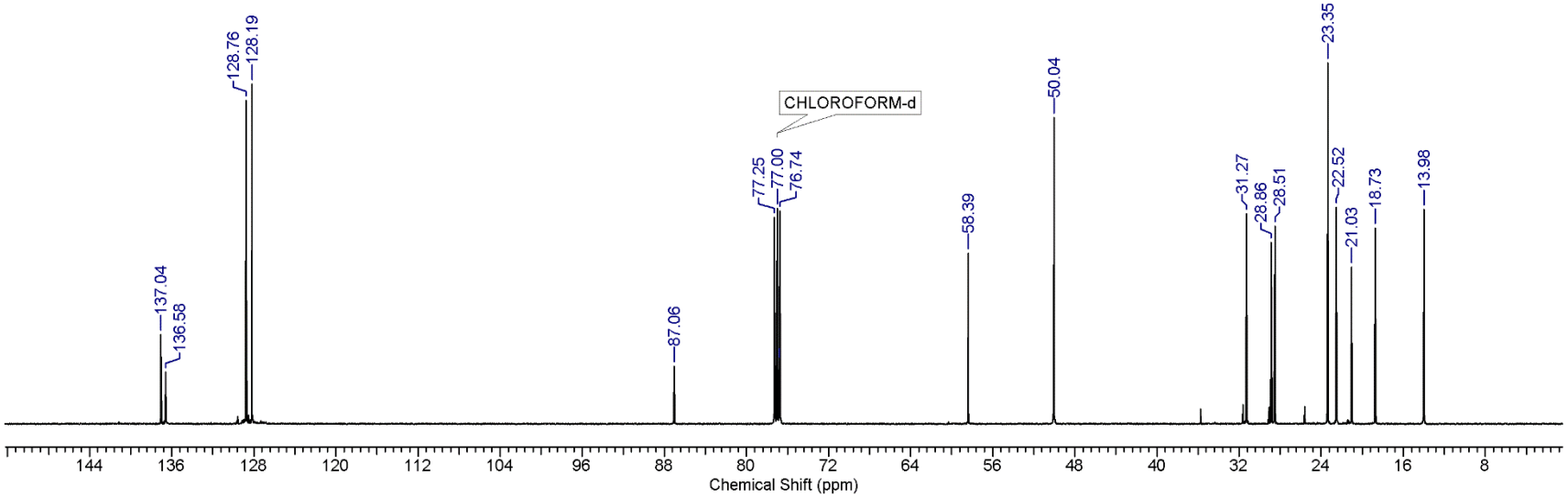

Me
N
H
3p
128.31
127.54
127.47
126.93
140.94
139.91
86.08
79.73
77.26
77.00
76.75
CHLOROFORM-d
53.21
50.97
31.31
28.84
28.56
22.55
18.82
14.02
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

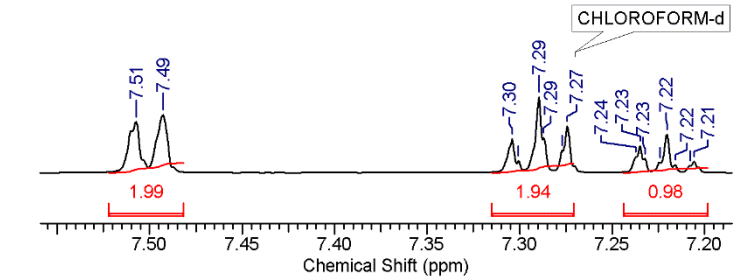

Me
N
Me
3q
CHLOROFORM-d
Chemical Shift (ppm)
Chemical Shift (ppm)

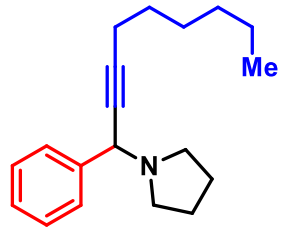

CHLOROFORM-d
77.25
77.00
76.82
76.74
77.5
77.0
76.5
Chemical Shift (ppm)


Me
N
Me

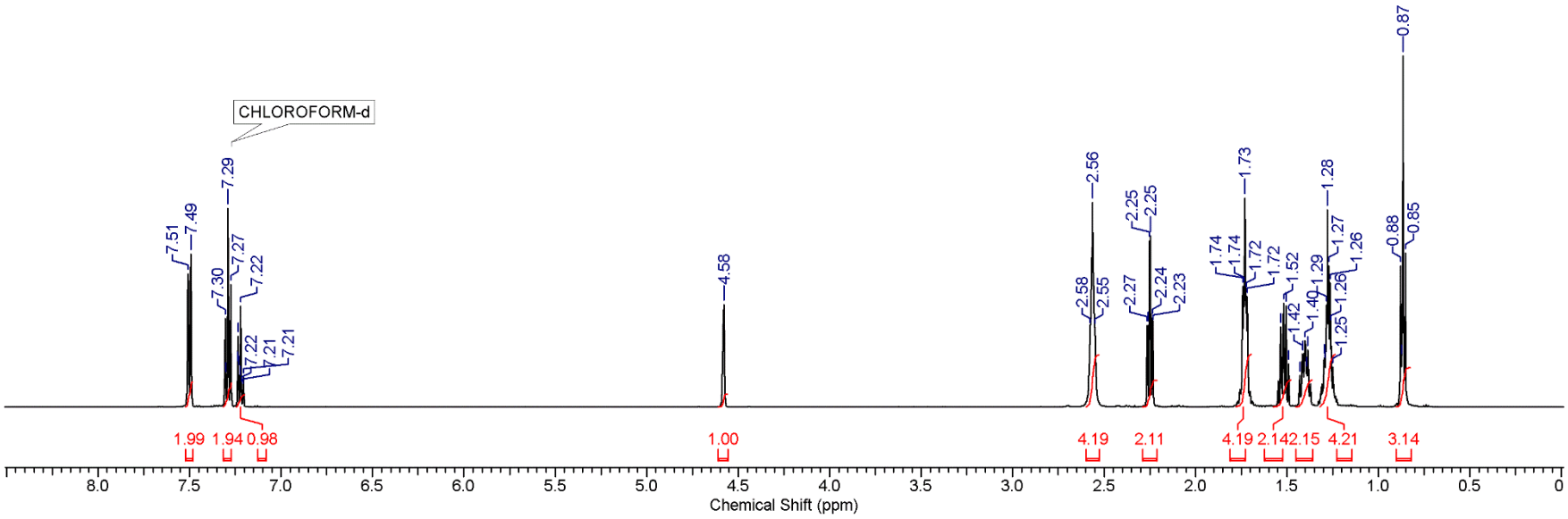
3q

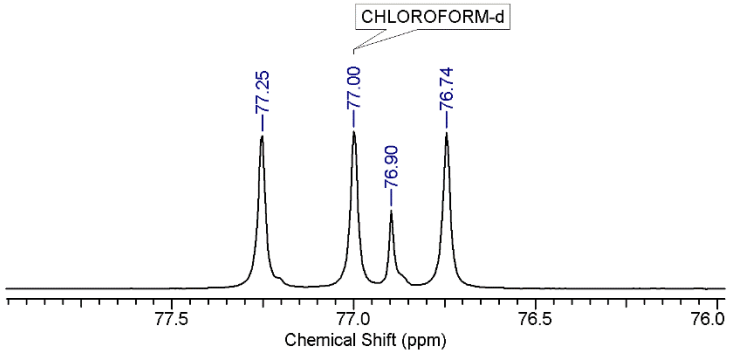

137.04
136.58
128.76
128.19
87.06
CHLOROFORM-d
77.25
77.00
76.74
58.39
50.04
31.27
28.86
28.51
23.35
22.52
21.03
18.73
13.98
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

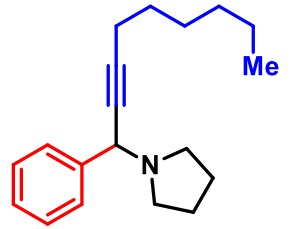

CHLOROFORM-d
7.51
7.49
7.30
7.29
7.29
7.27
7.24
7.23
7.23
7.22
7.22
7.21
1.99
1.94
0.98
7.50
7.45
7.40
7.35
7.30
7.25
7.20
Chemical Shift (ppm)


Me
N

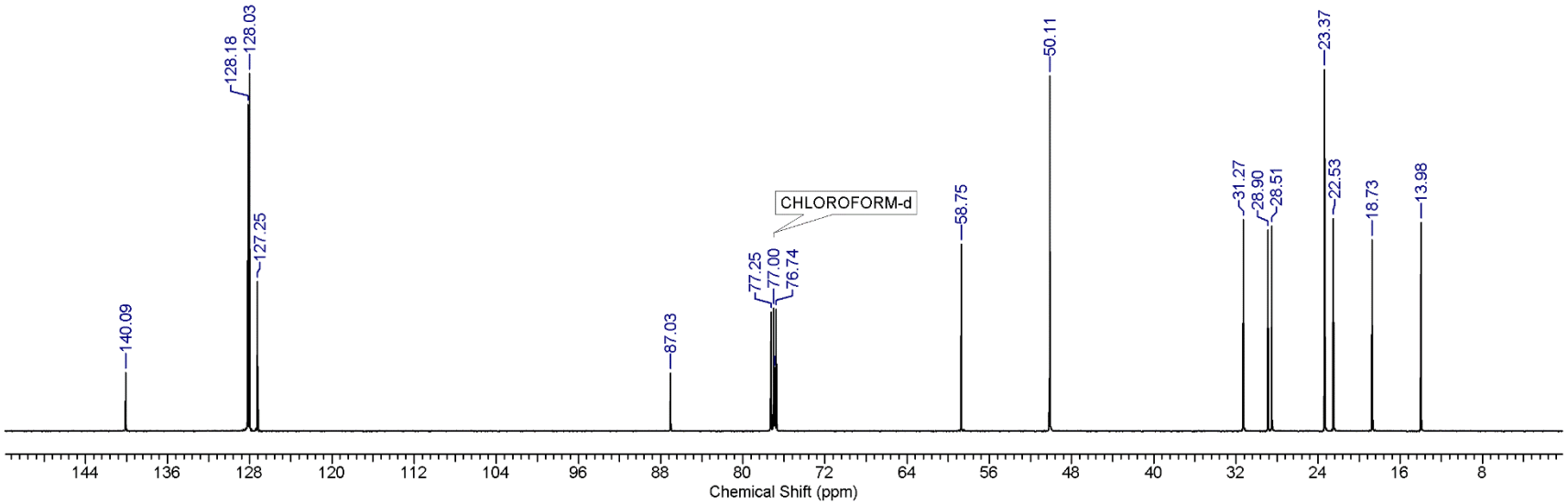
**3r**


CHLOROFORM-d
7.51
7.49
7.29
7.30
7.27
7.22
7.22
7.21
7.21
4.58
2.58
2.56
2.55
2.27
2.25
2.25
2.24
2.23
1.74
1.74
1.73
1.72
1.72
1.52
1.42
1.40
1.29
1.28
1.27
1.26
1.26
1.25
0.88
0.87
0.85
1.99
1.94
0.98
1.00
4.19
2.11
4.19
2.14
2.15
4.21
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CHLOROFORM-d
77.25
77.00
76.90
76.74
77.5
77.0
76.5
76.0
Chemical Shift (ppm)


Me
N

**3r**


128.18
128.03
127.25
140.09
87.03
CHLOROFORM-d
77.25
77.00
76.74
58.75
50.11
31.27
28.90
28.51
23.37
22.53
18.73
13.98
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)